Journal

of the

Indian Chemical Society

June, 1960

1960 Vol. XXXVII No. 6

Published by the Indian Chemical Society
92, Acharya Prafulla Chandra Road, Calcutta-9.

"SIGCOL"

LABORATORY GLASSWARE

Made of

BOROSILICATE GLASS HAVING HIGH SILICA AND LOW ALKALI CONTENT WHICH ENSURES RESISTANCE TO THERMAL SHOCK AND CHEMICAL STABILITY

SARTORIUS

"SELECTA" BALANCES

Micro and Projection Types

CARL-ZEISS

REFRACTOMETERS

SPECTROPHOTOMETERS

STEREO-MICROSCOPES

MUIRHEAD

POTENTIOMETER

"K-9"

TRIANGULAR BEAM

CIRCULAR ARRESTMENT

ANALYTICAL BALANCE

CAPACITY : 200 Gms.

SENSITIVITY : 1/10 Mgm.

5 Divisions throw of pointer for addition of 1 Mgm.

CARL-ZEISS

HAND SPECTROSCOPES

POLARISING MICROSCOPES

METAL MICROSCOPES

POLARIMETERS

MICRO-PHOTO CAMERAS

LEYBOLD'S

VACUUM PUMPS

HEREAUS - OVENS

JULIUS PETER - BOMB CALORIMETER

HOPPLER - VISCOMETERS

Distributors :

ADAIR, DUTT & Co. (INDIA) PRIVATE Ltd.

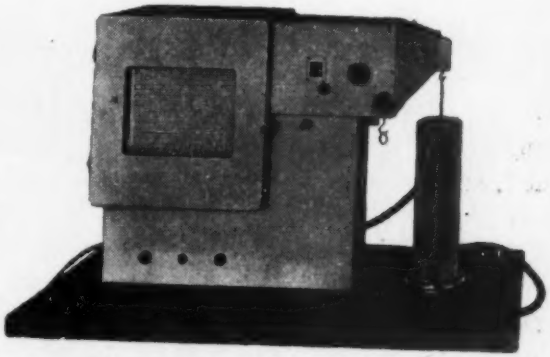
CALCUTTA MADRAS BOMBAY NEW DELHI

SARTORIUS

ORIGINAL SARTORIUS SEDIMENTATION BALANCE

An automatic instrument for the determination of the particle-size distribution.

THE ORIGINAL SARTORIUS Sedimentation Balance was developed in close co-operation with Dr. Bachmann for the determination of particle-sizes. This balance records the increase in weight of a sediment deposited on the pan as a function of time. In this way the grain size distribution curve of the sediment can be deduced from the curve obtained. Particle sizes between 1 and 60 microns, which are usually outside the range of a screen analysis, can be determined by this method.



Sedimentation Balance

For further particulars please write to :—

Sole Distributors

THE SCIENTIFIC INSTRUMENT COMPANY LIMITED

ALLAHABAD • BOMBAY • CALCUTTA • MADRAS • NEW DELHI

Announcing an Historic Breakthrough in Chemical Documentation

INDEX CHEMICUS

A new approach to the problem of handling chemical literature now makes it possible to index new chemical compounds within 30 days after their appearance in the primary journals.

We are proud to announce the publication of the **INDEX CHEMICUS,** a monthly register and index of more than 50,000 new chemical compounds — estimated to be at least 95% of all synthesized each year throughout the world.

Existing chemical indexes are appearing two to four years late and the time lag has been increasing. This delay has been eliminated in the **INDEX CHEMICUS** through the development of new indexing techniques utilizing unique manual and machine methods for handling scientific information.

INDEX CHEMICUS will contain listings of chemical names, structural diagrams, and molecular formulas as well as complete bibliographical information. Indexes will be cumulated quarterly and yearly.

For detailed information and specimen pages, contact:

INSTITUTE FOR SCIENTIFIC INFORMATION

1122 Spring Garden Street

Philadelphia 23, Pennsylvania

JOURNAL OF THE INDIAN CHEMICAL SOCIETY

JUNE, 1960

Contents

		Page
59.	Solvent effect on the ultraviolet absorption spectra of sulphoxides. Part I.—By V. Baliah and R. Varadachari	321
60.	Kinetics of the alkaline hydrolysis of chloroform in ethanol.—By Sameer Bose ..	325
61.	Ionic reactions in thionyl chloride. Part I. Complexes of solvo-acids and ansolvo-bases.—By Sarjit Singh Sandhu, Bhupinder Singh Chakkal and Gurmit Sarjit Sandhu	329
62.	Occurrence of auraptene, umbelliferone, marmin, lupeol and skimmianine in the root of *Aegle marmelos* Correâ—By Mrs. A. Chatterjee and B. Chaudhury	334
63.	Dependence of optical activity on chemical constitution. Part I. Salts of acetic, propionic, butyric, phenylacetic, β-phenylpropionic and cinnamic acids with cinchonidine.—By Maghar Singh Manhas and Kali Kumar Shukla ..	337
64.	Compounds of cadmium bromide and iodide with amines and heterocyclic bases.—By Sarju Prasad, K. S. R. Krishnaiah and T. Ranganathachar	344
65.	Complex compounds of stannous bromide with amines and heterocyclic bases.—By Sarju Prasad, K. S. R. Krishnaiah and V. Hariharan	347
66.	The apparent dissociation constants of diethyldithiocarbamic acid.—By K. P. Soni and A. M. Trivedi	349
67.	Thiazolidones. Part IV. Synthesis of 2-aryl-3-benzyl-4-thiazolidones.—By B. K. Raval and J. J. Trivedi	353
68.	Thiazolinylhydrazones. Part I. Synthesis of 4-oxo-5-(aryl)-Δ^2-thiazolin-2-ylhydrazones.—By P. R. Pathan, B. K. Raval and J. J. Trivedi ..	355
69.	Synthesis in the 3-azafluorene group. Part II. A new synthesis of 3-azafluorenone.—By J. N. Chatterjea and K. Prasad	357
70.	Chalkones. Part III. Synthesis of methylchalkones.—By Durga Nath Dhar ..	363
71.	Organic pesticides. Part I. Preparation of some fluoroaryloxy fatty acids and their mercury derivatives.—By K. C. Joshi and S. C. Bahel	365
72.	Possible antituberculous compounds. Part VIII. Preparation of diphenylamine-4-aryl- or -alkyl-amidines.—By Vinay S. Misra and Md. Imtiaz Husain ..	367
73.	Polycyclic systems. Part VIII. Synthesis of seven-membered ring compounds.—By D. Nasipuri, R. Roy and U. Rakshit	369
	Obituary	376
	Review	377

Information for Authors

1. All papers intended for publication in the Journal of the Indian Chemical Society should be addressed to the Hony. Secretary, Indian Chemical Society, 92, Acharya Prafulla Chandra Road, Calcutta-9.

2. *A paper will not normally be considered for publication in the journal unless at least one of the author or authors is (are) either a Fellow or Associate member of the Society.*

3. Communications which have appeared in any other journal shall not be published in this Journal unless this course is specially approved by the Council.

4. Normally an article or original paper should not exceed 15 foolscap pages. *All papers should be submitted in duplicate in typescript* with double line and marginal spacings. Tables and foot notes add considerably to the cost of printing ; authors are requested therefore not to use them unless necessary.

5. *All papers should be carefully revised and should be absolutely in final form of printing.* Positions for text-figures should be indicated. Authors are particularly requested to verify references. Authors are solely responsible for the factual accuracy of their papers.

6. Authors should note that the communications are meant for specialists in that field. Extensive review of literature should be avoided. Well-known or previously published procedures followed in the experimental work should only be designated or referred to.

7. Periods of time (unless fractional) and quantities of material should be written in numerals. For economy the abbreviations, cm, c.c., g., m.p., b.p., f.p., calc., exp., Fig., etc., should be used.

8. Authors are requested to enclose line drawings of the diagrams in their papers drawn in India ink on smooth white Bristol board. The drawings should be twice the size they will occupy in the Journal. Authors are particularly requested to reduce the number of diagrams and formulae to an absolute minimum. Organic structural formulae should be arranged to fill the space economically and arrows should be used horizontally or vertically, not diagonally, whenver possible.

9. The reference to literature should be given in brackets in the text and not as a foot-note or at the end and should conform to the normal usages of the *Journal* as regards order and punctuations, and to the abbreviations as given by Chemical Abstracts in its "List of Periodicals Abstracted". Thus, Name or names of authors, Name of Journal (abbreviated, with a single underline ; year of publication ; number of volume (double underline) and lastly page, e.g., Karrer and Schlieutz, *Helv. Chim. Acta*, 1934, **17**, 7.

The words and lines that will appear in italics in print should be underlined.

10. Authors are expected to be familiar with the normal rules of nomenclature but in case of doubt may refer to "Modern Chemical Nomenclature (Smith, *J. Chem. Soc.* 1936, 1067).

11. New compounds should be indicated by underlining the name at its first mention (excluding Headings) in the experimental section and by giving analytical results in the form : "(Found :———; ———. ——— requires———%)" Analytical results for compounds which have been previously known should be given in the form : "(Found :———; ———. Calc. for ———; ———; ———%)".

12. *Every paper must be accompanied by a short abstract* giving briefly the objects of the investigation, the results obtained and their bearing on chemical knowledge in general. It should be such as to enable any chemist to obtain a clear idea of the investigation and normally should not exceed 250 words.

13. The address to which the proofs are to be sent should be written on every paper. One slip-proof or if possible a page-proof will be sent to authors, *which should be returned within a week to the Hony. Secretary, failing which it will be directly printed.*

14. Authors will get 50 copies of reprints free of charge and extra 25 copies on payment of Re. 1/- per page. Extra copies of reprints over 75 copies will be charged at Rs. 5/- per page. Cost of paper and binding, extra. If extra copies are required, the author should intimate the Hony. Secretary, at the time of returning the corrected proofs.

15. Notes will be given priority in publication.

HCA

SCHWEIZERISCHE
CHEMISCHE GESELLSCHAFT
Verlag Helvetica Chimica Acta
Basel 7 (Schweiz)

Seit 1918 **41** Jahre

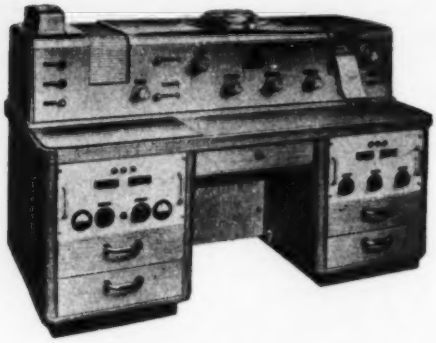
HELVETICA CHIMICA ACTA

Abonnemente : Jahrgang 1959, Vol. XLII = $ 25.–
Jahrgang 1960, Vol. XLIII = $ 25.–

Es sind noch lieferbar :
Neudruck zum Teil ab Lager
Vol. I—XXVII (1918—1944)
Originalausgaben, druckfrisch oder antiquarisch, Vol. XXVIII—XLI (1945—1958)
Diverse Einzelhefte ab Vol. I
Preise auf Anfrage Nur solange Vorrat

Das wissenschaftliche Organ der SCHWEIZERISCHEN CHEMISCHEN GESELLSCHAFT

ZEISS ALL-AUTOMATIC INFRA-RED SPECTROPHOTOMETER UR-10



Salient Features:

1 SPECTRAL RANGE 2 to 25 μ with three PRISMS

2 AUTOMATIC PRISM CHANGE

3 AUTOMATIC SPEED SUPPRESSION OF REGISTRATION FOR OPTIMAL RESOLUTION

4 PRE-SETTING TYPE DIAL SELECTOR FOR RECORDING THE REQUIRED SPECTRAL RANGES

CARL ZEISS JENA

VEB CARL ZEISS JENA

Sole Agents in India :

GORDHANDAS DESAI PRIVATE LTD.

PHEROZESHAH MEHTA ROAD, BOMBAY-1.

Branches :

P-7, Mission Row Extension, CALCUTTA 1.

4/2B, Asaf Ali Road, NEW DELHI.

22, Linghi Chetty Street, MADRAS 1.

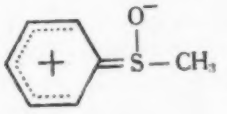
[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

SOLVENT EFFECT ON THE ULTRAVIOLET ABSORPTION SPECTRA OF SULPHOXIDES. PART I

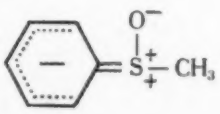
By V. Baliah and R. Varadachari

The ultraviolet absorption spectra of several sulphoxides in both ethanol and *cyclo*hexane (or hexane[n]) are recorded and an attempt has been made to explain the observed solvent effects.

The ultraviolet absorption spectra of sulphoxides have been studied, notably by Bordwell and Boutan (*J. Amer. Chem. Soc.*, 1957, **79**, 717) and Leandri *et al.* (*J. Chem. Soc.*, 1957, 1386). But the study cannot be said to be exhaustive. Many points of interest yet remain to be elucidated. The sulphinyl group may be assumed to resemble either the sulphonyl or the sulphide group. The comparison to the sulphonyl group can be justified from the existence of the common sulphur—oxygen bond. The comparison to the sulphide group can be justified from the existence of the $3s^2$ lone pair of electrons. When electronic excitation occurs in a sulphoxide like methylphenyl sulphoxide, either structure (I) or (II) should contribute to the excited state. If the sulphoxide behaves like methylphenyl sulphone, excitation leads to a greater contribution of (I). If it behaves like methylphenyl sulphide, (II) is the contributing structure to the excited state. From the spectral data, recorded by Price and Hydock (*J. Amer. Chem. Soc.*, 1952, **74**, 1943) and Bordwell and Boutan (*loc. cit.*), the view that the methylsulphinyl group enters into electron-donor type of conjugation in the photo-excited state, may be accepted.



(I)



(II)

We have undertaken an extensive study of the ultraviolet spectra of sulphoxides with a view to obtaining information on the following points : (1) the mode of electronic excitation in the derivatives of methylphenyl sulphoxide, (2) the mode of electronic excitation in diphenyl sulphoxide and its derivatives, (3) the effect of bulky *ortho*-substituents on the sulphoxide conjugation, (4) the possibility of chelation occurring in *o*-hydroxy sulphoxides, and (5) the effect of solvent. The present paper deals with the effect of solvent. In Table I are recorded the spectral data for methyl-, ethyl-, propyl^t- and butyl^t-phenyl sulphoxides.

TABLE I

(Wave-lengths in mμ)

Sulphoxide.	*cyclo*Hexane.		Ethanol (95%).	
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$
Methylphenyl	253	4,000	237	4,100
Ethylphenyl	253	3,700	240	4,200
Propyl^{t}phenyl	257	3,700	244	4,500
Butyl^{t}phenyl	263	3,800	251	4,200

The absorption maximum occurs at a longer wave-length in *cyclo*hexane (non-polar solvent) than in ethanol (polar solvent), the difference in wave-lengths being as much as 12 – 15 mμ. This is rather interesting because the solvent effect on the absorption spectra of sulphones is negligible (Baliah and Shanmuganathan, *J. Phys. Chem.*, 1958, **62**, 255). To emphasise the uniqueness of the sulphoxides in this respect, the spectral data for some alkylphenyl sulphides and alkylphenyl sulphones in hexane* and ethanol are shown in Table II for comparison.

TABLE II

(Wave-lengths in mμ)

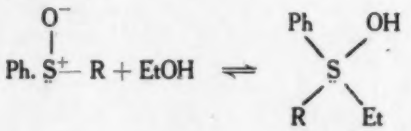
Compound.	Hexane*.		Ethanol (95%).	
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$
Methylphenyl sulphide	255*	6,900	254	9,500
Ethylphenyl sulphide	256	7,200	256**	7,900
Propyl[i]phenyl sulphide	..	..	258**	5,600
			215**	8,700
Butyl[i]phenyl sulphide	268	1,300	266**	1,500
	219	11,400	218**	12,000
Methylphenyl sulphone	217*	7,000	217	6,700
Bultyl[i]phenyl sulphone	213	8,400	216	8,700

*In *cyclo*hexane.

Data from Fehnel and Carmack (*J. Amer. Chem. Soc.*, 1949, **71, 84).

It is seen that the solvent effect is negligible for sulphides and sulphones. For ketones, considerable bathochromic shifts of absorption maxima occur on changing the solvent from *cyclo*hexane to ethanol—just the reverse of what happens in the case of sulphoxides. An explanation was offered by Baliah and Shanmuganathan (*loc. cit.*) for the effect of solvent on the spectra of sulphones and ketones. The blue shift, which occurs for alkylphenyl sulphoxides on changing the solvent from *cyclo*hexane to ethanol, indicates that the ground states are more stabilised in ethanol than in *cyclo*hexane because it is not probable that their excited states are more stabilised in *cyclo*hexane than in ethanol.

The greater stabilisation in ethanol cannot be merely due to hydrogen-bond formation, for then a similar behaviour should be observable in the case of sulphones also. A possible explanation for the greater stability of alkylphenyl sulphoxides in ethanol towards electronic excitation is that these are solvated in ethanol as follows :



(III)

There can be no objection to structure (III) because sulphur is known to utilise its vacant 4*s*- or 3*d*-orbitals (Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 231 ; Baliah *et al.*, *J. Phys. Chem.*, 1957, **61**, 1013 ; Baliah and Miss Uma, *Naturwiss.*, 1958, **45**, 512 ; Varadachari, Ph.D. thesis, Annamalai University, 1959). The solvent interaction postulated for sulphoxides is not possible for sulphides and sulphones.

In contrast to alkylphenyl sulphoxides, diaryl sulphoxides show a different solvent effect. The absorption maxima of diaryl sulphoxides occur at longer wave-lengths in ethanol than in *cyclo*hexane (see Table III).

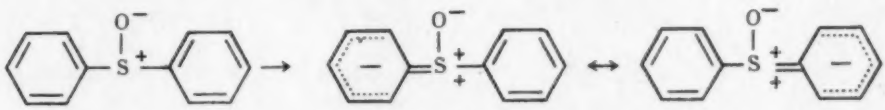
TABLE III

(Wave-lengths in mμ)

Sulphoxide.	*cyclo*Hexane.		Ethanol (95%).	
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$
Diphenyl	227	12,600	232.5	13,700
2-Methyldiphenyl	228*	11,800	235*	14,500
4-Methyldiphenyl	233*	11,200	238	16,500
2-Methoxydiphenyl	..	..	235	13,500
			285	4,100
4-Methoxydiphenyl	248	16,100	248	17,100
4-Nitrodiphenyl	261	11,100	265	11,100
4 : 4′-Dimethyldiphenyl	237*	15,800	240	19,000
4 : 4′-Dimethoxydiphenyl	..	..	251	23,000
2-Chlorodiphenyl	230*	13,500	235*	14,800
4-Chlorodiphenyl	234*	15,800	239*	18,200
4 : 4′-Dibromodiphenyl	248*	21,900	249	22,500

*Data from Leandri *et al.*, *loc. cit.*

The solvent effect on the spectra of diaryl sulphoxides indicates that the excited states of these compounds should be more stabilised in ethanol than in *cyclo*hexane. This can be explained if the electronic excitation is supposed to occur in the following way :



The magnitude of the ionic charge is greater in the excited state and, hence, there will be greater stabilisation of the excited state in ethanol due to greater solvation. Then the following question naturally arises : why should not the kind of solvation postulated for the alkylphenyl sulphoxides in the ground state be postulated for the diaryl sulphoxides also ? The answer to this question seems to be that the diaryl sulphoxides are stabilised in the ground state to a greater extent than the alkylphenyl sulphoxides due to increased resonance resulting from the presence of two benzene nuclei. The resonance energy thus resulting should be greater than solvation energy that can result from solvation of the type postulated in the case of alkylphenyl sulphoxides.

EXPERIMENTAL

All the sulphoxides used in the present investigation, excepting the new ones specified below, were prepared as described in the literature.

Phenylpropyl Sulphoxide.—To a solution of phenylpropyl sulphide (5 g.) in acetic acid (80%, 75 c.c.) at 60° was added a saturated aqueous solution of chromic anhydride (2.4 g.). The mixture was heated for 20 mins. at 60–70°. After cooling it was poured on ice-water, extracted with ether, and dried with anhydrous sodium sulphate. After distilling off the ether, the sulphoxide boiled at 127°/7 mm, yield 2 g. (Found : C, 64.09 ; H, 7.34. $C_9H_{12}OS$ requires C, 64.27 ; H, 7.19%).

Phenylbutyl^t*sulphoxide* was prepared by the oxidation of phenylbutyl^t sulphide (de la Mare and Vernon, *J. Chem. Soc.*, 1956, 41) (4 g.) with hydrogen peroxide (30%, 7 c.c.) in the usual way. The yield was 2 g. The sulphoxide, after a number of recrystallisations from ethanol, melted at 58-59°. (Found : C, 65.73 ; H, 7.83. $C_{10}H_{14}OS$ requires C, 65.88 ; H, 7.74%).

2-Methoxydiphenyl Sulphoxide.—2-Methoxydiphenyl sulphide (Mauthner, *Ber.*, 1906, **39**, 3595) (2.7 g.) was dissolved in glacial acetic acid (25 c.c.) and mixed with an aqueous solution of chromic anhydride (0.9 g.). The mixture was heated for 20 mins. at 60–70°, cooled and poured on crushed ice. A solid gradually separated. It was removed by filtration. After four recrystallisations from ethanol it melted at 96-97°, yield 1 g. (Found : C, 67.33 ; H, 5.25. $C_{13}H_{12}O_2S$ requires C, 67.19 ; H, 5.21%).

4-Methoxydiphenyl Sulphoxide.—4-Methoxydiphenyl sulphide (2.7 g.) was oxidised with an aqueous solution of chromic anhydride (0.9 g.) as described for the foregoing compound. The yield was 0.8 g. After a number of recrystallisations from methanol, the sulphoxide melted at 68-69°. (Found : C, 67.25 ; H, 5.71. $C_{13}H_{12}O_2S$ requires C, 67.19 ; H, 5.21%).

Ultraviolet Absorption Measurements.—The ultraviolet absorption spectra were determined with a Beckman quartz spectrophotometer, model DU. Ethanol was purified by distillation after treatment with lead acetate and sodium hydroxide. *cyclo*Hexane was purified by distillation after passing repeatedly through a column of silica gel. Hexane^n was purified by the method of Castille and Henri (*Bull. Soc. Chim. biol.*, 1924, **6**, 299 ; *Chem. Abst.*, 1924, **18**, 3165).

The authors wish to thank the Government of India for the award of a research scholarship to one of them (R.V.).

Department of Chemistry,
Annamalai University,
Annamalainagar.

Received October 5, 1959.

[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

KINETICS OF THE ALKALINE HYDROLYSIS OF CHLOROFORM IN ETHANOL

By Sameer Bose

The order of the reaction, as determined by isolation and integration methods, has been found to be 2, when alkali concentration is not more than 2 or 3 times that of chloroform. Specific rate constants evaluate between 20° and 40°. The Arrhenious energy of activation, determined graphically, is 33.3 K. cals. in 95% ethanol. In presence of a large excess of alkali, the order has been found to increase to 3.

Saunders (*J. Phys. Chem.*, 1900, **4,** 660) found the rate of hydrolysis of chloroform by alkali in 95% ethanol to be of first order with respect to both hydroxide and chloroform concentrations. Abel (*Z. Elektrochem.*, 1923, **29,** 391) reported that in very dilute solutions the reaction was of the first order, being independent of alkali concentration, but with an increase in alkali concentration the order was found to increase. Hine (*J. Amer. Chem. Soc.*, 1950, **72,** 2438) using aqueous dioxane solutions found the reaction to be bimolecular. In view of this divergence in kinetic order, the present investigation was undertaken, using 95% ethanol solutions. An analytical study of this reaction (Bose, this *Journal*, 1949, **36,** 554) reveals that two simultaneous reactions take place during alkaline hydrolysis :

(*i*) $CHCl_3 + 4\,KOH = HCOOK + 3\,KCl + 2\,H_2O$

(*ii*) $CHCl_3 + 3\,KOH = 3\,KCl + 2\,H_2O + CO$

At temperatures below 45°, the first reaction is predominant while at higher temperatures, the second one occurs to a larger extent, involving the evolution of a large quantity of carbon monoxide. Hence, a kinetic study was undertaken at temperatures below 45°.

Experimental

A standard solution of chloroform was prepared by weighing the Analar variety of the reagent and dissolving it in absolute ethanol (C.P.). The alkali was dissolved in minimum quantity of water and diluted with the same solvent. This solution was standardised with 0.05*N*-HCl after keeping for 24 hours and then used. In most of the experiments the reaction was followed by estimating the KOH content by titration with HCl (0.05*N*) to phenolphthalein end-point. In presence of a large excess of alkali, the KCl produced was evaluated by Vohlard's method. The reaction was stopped in all the experiments by acidifying the solution with HCl or HNO_3. In some experiments, a large quantity of KCl precipitated out which made pipetting difficult. This difficulty was overcome by thermostatting aliquoted portions.

Order of Reaction.—The velocity of reaction may be represented by the equation :

$$-dc/dt = k.C_1^m\,C_2^n \qquad .. \qquad .. \quad (1)$$

where C_1 and C_2 represent respectively the concentration of KOH and $CHCl_3$. In the following series of experiments, a large excess of chloroform was used so that during the course of the reaction its concentration diminished by about 1.5%, whereas that of KOH to less than half. Hence, the concentration of the former may be taken as practically constant. The velocity equation then takes the following form :

$$-dc/dt = (kC_2^n)\,C_1^m = k_1 C_1^m \qquad .. \qquad .. \quad (2)$$

where $k_1 = kC_2^n$. The order of the reaction is the same as m. It appears from Table I that the values of k_1 calculated for $m = 1$ exhibit such a degree of constancy that the equation indicating a unimolecular order with respect to KOH may be regarded as the appropriate one.

TABLE I

Apparent first-order rate constants in presence of excess of $CHCl_3$.

Initial conc. of $CHCl_3 = 1.25M$. Temp. = 25°.

Time (min.)	..	..	0	10	32	79	133	199	300
KOH conc. ($N \times 200$)	..	..	9.5	9.0	8.0	6.8	5.4	4.2	2.7
$k \times 10^4$ (unimol.)	..	..	..	41.7	42.7	42.3	42.5	41.2	41.9
Mean $k \times 10^4$	..	..		at 25.°		at 30.°		at 35.°	
				42.0		81.9		178.0	

Determination of n.—Supposing in equation (2) k'_1 and k''_1 are the two values of k_1 (in the equation $k_1 = kC_2^n$) obtained in two experiments in each of which C_1, the initial concentration of KOH, is the same whilst the concentrations of chloroform are different; say C'_2 and C''_2, the following equations are obtained:

$$k'_1 = kC'^n_2 \quad .. \quad .. \quad (3)$$

$$k''_1 = kC''^n_2 \quad .. \quad .. \quad (4)$$

If logarithms are taken and results subtracted, it is found, that

$$n = \log \frac{k'_1}{k''_1} \Big/ \log \frac{C'_2}{C''_2} \quad .. \quad .. \quad (5)$$

The values of k'_1 and k''_1 have been found by assuming $m = 1$ in the velocity equation (2). The results are recorded in Table II.

TABLE II

Apparent first-order constants in presence of two diff. conc. of $CHCl_3$ *(in excess).*

Temp.	Initial conc. of $CHCl_3 = 0.6\ M.$ Mean $k'_1 \times 10^4$ min.$^{-1}$	Initial conc. of $CHCl_3 = 1.2\ M.$ Mean $k''_1 \times 10^4$ min.$^{-1}$
25°	16.2	34.4
30°	36.0	74.0
35°	75.0	163.0

By combining the above results, the actual values of n found are 1.08, 1.03 and 1.12 at 25°, 30° and 35° respectively. n appears to approach very closely to the value 1. Hence, the reaction in presence of excess of chloroform is unimolecular with respect to both the reacting substances.

Values of n and m in presence of excess of KOH.—Using a large excess of KOH and assuming $n = 1$ in equation (1), unimolecular constants were calculated. The constancy of the values obtained indicates a unimolecular order with respect to $CHCl_3$. By using two different concentrations, C'_1 and C''_1 for KOH (in excess) (cf. Table III), the value of m was calculated according to equation (5), substituting m for n and C_1 for C_2. Strangely enough, the values of m found were 1.97 and 1.96 at 25° and 30° respectively. Therefore in presence of excess of KOH, the reaction is unimolecular with respect to $CHCl_3$ and bimolecular with respect to KOH. This is in agreement with the observations of Abel (*loc. cit.*) who reports that the order with respect to KOH increases with increase in its concentration.

TABLE III

Apparent first-order rate constants in presence of two diff. conc. of KOH *(in excess).*

* A. KOH = 2.4 *N*. $CHCl_3$ = 0.02 *M*.		* B. KOH = 1.2 *N*. $CHCl_3$ = 0.02 *M*.	
Temp.	Mean $k_1'' \times 10^4$ min.$^{-1}$		Mean $k_1' \times 10^4$ min.$^{-1}$
25°	107		27.4
35°	444		114.0

* Refers to initial concentrations of the reactants.

Bimolecular Rate Constants.—The stoichiometric equation for the reaction at lower temperatures is

$$A + 4B = 3C + D.$$

When a, b, $a - x/4$ and $b - x$ are the initial and instantaneous concentrations of $CHCl_3$ and KOH respectively, the rate equation is

$$dx/dt = k(a - x/4)(b - x).$$

The integrated form is

$$kt = \frac{4}{b - 4a} \cdot \ln \frac{a(b - x)}{b(a - x/4)} \quad .. \quad (6)$$

Taking dilute solutions of the two reactants in proportions other than stoichiometric, the rate of disappearance of alkali was found at different temperatures (20°-40°). A plot of log of $b - x/(a - x/4)$ against time was found to be a straight line as expected from equation (6). The rate constants, calculated for several temperatures and those at 35°, are shown in Table IV. The k was found to be fairly constant for a particular run. The effect of change in concentration and relative proportion of the reactants was also studied and a slight but distinct fall in k was noticed with decrease in the alkali concentration, as recorded in Table V.

TABLE IV

Bimolecular rate constants at 35° using diff. initial conc. of the reactants.

Time.	$b - x$ ($M \times 10^3$).	$a - x/4$ ($M \times 10^3$).	$k \times 10^4$. (l.mol^{-1}. $\times$ min^{-1}).	Time.	$b - x$. ($M \times 10^3$).	$a - x/4$ ($M \times 10^3$).	$k \times 10^4$. (l.mol$^{-1} \times$ min^{-1}).
0 min.	18.41	9.99	..	0 min.	9.205	4.992	..
60	16.74	9.57	163	60	8.814	4.890	137
120	15.29	9.20	162	121	8.423	4.835	141
226	13.16	8.68	162	242	7.825	4.653	140
317	11.59	8.32	164	318	7.490	4.576	139
403	10.40	8.01	162	405	7.098	4.472	138
499	9.20	7.69	162	500	6.680	4.370	153
617	7.90	7.36	163	1118	4.680	3.864	140
		Mean	162			Mean	141

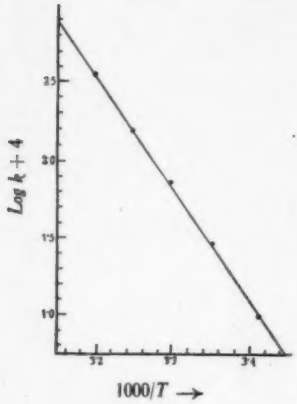
TABLE V

Effect of relative proportion and conc. of the reactants on k at 35°.

Ratio of $CHCl_3$: KOH. (Molality basis).	Initial conc. of KOH.	$k \times 10^4$ (l.mol^{-1}. min^{-1}).	Divergence from mean.
1 : 1.2	0.12 *N*	150	−5.0%
1 : 1.8	0.092	141	−11
1 : 1.8	0.14	158	Nil
1 : 1.8	0.19	162	+0.3
1 : 2.5	0.25	168	+5.0
1 : 3.7	0.28	169	+7.0
		Mean 158	

Temperature Dependence.—The effect of variation in temperature on the rate of the reaction was studied between 20° and 40° using the same initial concentration of the two reactants ($CHCl_3$, 0.1*M*; KOH, 0.2*M*). In Fig. 1, log k (bimolecular) has been plotted against $1/T$, and from the slope of the straight line obtained, the Arrhenius activation energy of 33.3 K. cals. was calculated. From the expressions of the transition state theory (Glasstone, Ering and Laidler, "Rate Processes", 1941, pp. 197, 417) the values of the heat and entropy of activation were computed for the reaction at 25° when $k = 5 \times 10^{-5}$ l.mole^{-1} sec.$^{-1}$ These quantities are $\Delta H = 32.7$ K.cals and $\Delta S = 44$ e.u.

FIG. 1



DISCUSSION

Hine (*loc. cit.*) has presented a strong case in favour of the view that the hydrolysis of chloroform by alkali commences with the extraction of the proton by the basic anion. The bimolecular reaction in ethanol also appears to follow the same mechanism :

$$CHCl_3 + OH^- \overset{\text{Fast}}{\rightleftharpoons} CCl_3^- + H_2O$$

$$CCl_3^- \xrightarrow{\text{Slow}} CCl_2 + Cl^-$$

$$CCl_2 \xrightarrow[H_2O]{OH^- \text{ fast}} HCOO^- + CO$$

The fact that the order of the reaction increases with the increase in alkali concentration is undeniable. In presence of a large excess of KOH, the termolecular reaction observed cannot be regarded as merely a medium effect. It is very likely that the hydroxyl ions, when in excess, not only extract a proton but substitute one of the halogen atoms by hydroxyl :

$$CHCl_3 + 2OH^- \overset{\text{Fast}}{\rightleftharpoons} C(OH)Cl_2^- + Cl^- + H_2O$$

$$C(OH)Cl_2^- \xrightarrow{\text{Slow}} Cl + C(OH)Cl$$

$$C(OH)Cl + OH^- \xrightarrow{\text{Fast}} C(OH)_2 + Cl^-$$

$$C(OH)_2 \xrightarrow{\text{Isomerises}} HCOOH$$

The formation of carbon monoxide, as indicated in the mechanism postulated by Hine (*loc. cit.*), was found to be negligible (Bose, *loc. cit.*) in presence of large concentrations of alkali This fact also lends support to the mechanism shown above.

The author wishes to thank sincerely Principal Umadas Mukerji for providing all the facilities.

DEPARTMENT OF CHEMISTRY,
M. M. V., JABALPUR.

Received November 10, 1959

[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

IONIC REACTIONS IN THIONYL CHLORIDE. PART I. COMPLEXES OF SOLVO-ACIDS AND ANSOLVO-BASES

BY SARJIT SINGH SANDHU, BHUPINDAR SINGH CHAKKAL AND GURMIT SARJIT SANDHU

Thionyl chloride, a polar solvent, has been employed as a medium for ionic reactions between ansolvo-bases and solvo-acids. Quaternary ammonium chlorides, such as, tetramethylammonium chloride, trimethylphenylammonium chloride, trimethylbenzylammonium chloride, dimethylphenylbenzylammonium chloride and triethylbenzylammonium chloride, react with solutions of titanium tetrachloride, zirconium tetrachloride and stannic chloride in thionyl chloride to yield normal complexes of the general formula :

$$\left[\begin{array}{c} R_3 \\ | \\ R_1 - N - R_2 \\ | \\ R_4 \end{array}\right]_2 MCl_6$$

The complexes of triethylbenzylammonium chloride with the aforementioned acids, which are highly soluble in thionyl chloride, have been separated out by the addition of dry ethyl acetate to the reaction mixture.

Formation of the complexes of zirconium tetrachloride with trimethylbenzylammonium chloride and triethylbenzylammonium chloride has also been studied by the conductometric method.

The formation of these complexes and changes in conductance have been explained on the basis of the ionisation of thionyl chloride and ionic species formed by the ionisation of ansolvo-bases and solvo-acids in thionyl chloride solutions.

Thionyl chloride possesses a fairly high value of dipole moment (1.60 *D* at 20° ; Beyaert and Govaert, *Chem. Abs.*, 1938, **32,** 6517), comparatively long and polar sulphur—chlorine bond (2.07 Å , expected 2.04 Å ; Palmer, *J. Amer. Chem. Soc.*, 1938, **60,** 2360 ; Allen and Sutton, *Acta Cryst.*, 1950, **3,** 46) and relatively high value of dielectric constant (9.25 at 20° ; Beyaert and Govaert, *loc. cit.*). It has a convenient working range of temperature (m.p.-104.5°, b.p. 78.8° ; Mayes and Partington, *J. Chem. Soc.*, 1926, 2594 ; Thorpe, *ibid.*, 1880, **37,** 141 ; 1882, **41,** 297) and its electrical conductivity (2.0×10^{-6} at 25° ; Walden, *Z. anorg. allgem. Chem.*, 1900, **25,** 209) is higher than that of acetyl chloride (4.0×10^{-7} at 25° ; Walden, *Z. physikal. Chem.*, 1906, **54,** 128). All these properties, which are comparable to those of other polar solvents, inspire a study of ionic reactions in this liquid. The ionisation of thionyl chloride has been indisputably established by conductometric and potentiometric work (Spandau and Brunneck, *Z. anorg. allgem. Chem.*, 1952, **270,** 201 ; 1955, **278,** 193). More recently the radioactive chlorine exchange studies have also confirmed (Masters *et al.*, *J. Amer. Chem. Soc.*, 1956, **78,** 4252) that ionisation of thionyl chloride can undoubtedly be expressed as :

$$SOCl_2 \rightleftharpoons SOCl^+ + \bar{Cl}.$$

In the present investigations, ionic reactions involving solvo-acids and ansolvo-bases have been studied. Titanium tetrachloride, stannic chloride and zirconium tetrachloride, which ordinarily possess tetrahedral structure (Lister and Sutton, *Trans. Faraday Soc.*, 1941, **37,** 393) have an inherent tendency to acquire more stable octahedral configuration by the acceptance of two chloride ions to form the ion MCl_6^{2-} (Dickinson, *J. Amer. Chem. Soc.*, 1922, **44,** 276). In thionyl chloride these chlorides dissolve to form solvo-acids of the type $MCl_4.2SOCl_2$. The existence of $TiCl_4.2SOCl_2$ has been reported on the basis of thermal analysis (Sheldon and Tyree, *ibid.*, 1959, **81,** 2290) while the formation of similar compounds by stannic chloride and zirconium tetrachloride is presumed in solution. Stannic chloride (Walden, *loc. cit.*, 1900) and titanium tetrachloride (Eingorn, *Ukrain Khim. Zhur.*, 1950, **16,** 404 ; *Chem. Abs.*, 1954, **48** 3775), which are non-conductors of electricity, have dipole moment almost equal to zero (Ulich *et al.*, *Z. physikal.*

Chem., 1932, **B17**, 369). However, these yield solutions in thionyl chloride which are much more conducting than the pure solvent (Spandau and Brunneck, *loc. cit.*, 1952). Zirconium tetrachloride dissolves in thionyl chloride to form a solution which is more conducting as compared to the pure solvent. The increase in electrical conductivity of their solutions in thionyl chloride may be explained on the basis of ionisation of the solvo-acids formed in solutions.

$$TiCl_4 + 2SOCl_2 \rightleftharpoons TiCl_4.2SOCl_2 \rightleftharpoons 2SOCl^+ + TiCl_6^{2-}$$

$$SnCl_4 + 2SOCl_2 \rightleftharpoons SnCl_4.2SOCl_2 \rightleftharpoons 2SOCl^+ + SnCl_6^{2-}$$

$$ZrCl_4 + 2SOCl_2 \rightleftharpoons ZrCl_4.2SOCl_2 \rightleftharpoons 2SOCl^+ + ZrCl_6^{2-}$$

The ansolvo-bases, which have been employed to study the complexes of these solvo-acids, are : tetramethylammonium chloride, trimethylphenylammonium chloride, trimethylbenzylammonium chloride, dimethylphenylbenzylammonium chloride and triethylbenzylammonium chloride. The mode of ionisation of these bases in thionyl chloride may be exemplified by tetramethylammonium chloride.

$$(CH_3)_4N.Cl \rightleftharpoons (CH_3)_4N^+ + Cl^-$$

Ordinarily the solutions of quaternary ammonium chlorides containing methyl groups and that of titanium tetrachloride in thionyl chloride react to form yellow precipitates when the amounts of ansolvo-bases and the solvo-acid are taken in a molar ratio of 2 :1 respectively. However, triethylbenzylammonium chloride and titanium tetrachloride in thionyl chloride react to yield a clear solution, and even on cooling, no solid separates. Fortunately, the addition of dry ethyl acetate helps in obtaining a solid mass which is filtered and kept under vacuum to remove the last traces of the solvents. Its analysis led to the composition of the normal complex $[(C_2H_5)_3N.C_7H_7]_2TiCl_6$. The formation of these acid-base complexes is explained on the basis of ionic species which already exist in thionyl chloride solutions. For instance, the formation of $[(CH_3)_4N]_2TiCl_6$ may be represented as :

$$2(CH_3)_4N^+ + 2SOCl^+ + 2Cl^- + TiCl_6^{2-} \rightarrow [(CH_3)_4N]_2TiCl_6 + 2SOCl_2.$$

The precipitation of the normal complex helps the reaction to proceed to completion.

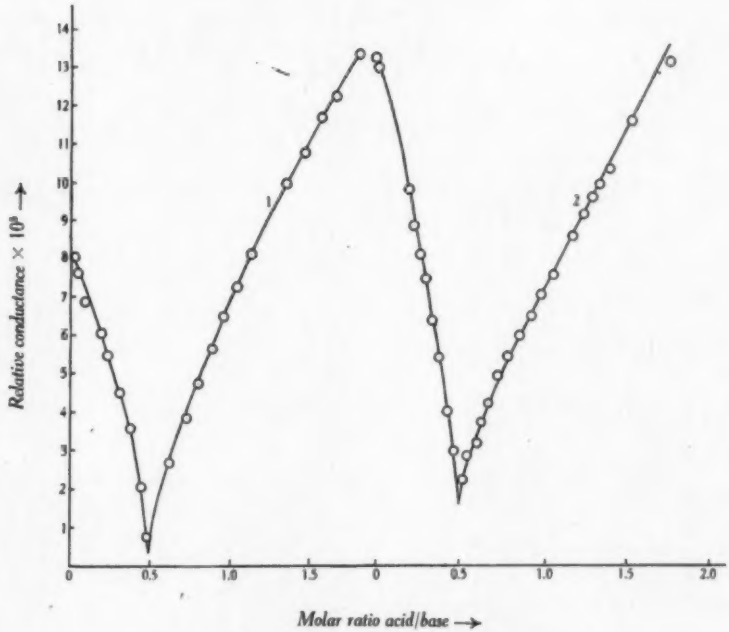
Zirconium tetrachloride, which is fairly soluble (1-2%) in thionyl chloride, reacts with the quaternary ammonium chlorides, excepting triethylbenzylammonium chloride, in thionyl chloride to yield precipitates of the normal complexes. However, the striking influence of ethyl group on the solubility of the normal complex of zirconium tetrachloride and triethylbenzylammonium chloride in thionyl chloride is illustrated by the non-precipitation of the complex when the reactants are mixed together. Here again, dry ethyl acetate has been used to precipitate out the normal complex. Nevertheless, doubt may be entertained regarding the formation of this normal complex as both of the reactants are ordinarily solids and dry ethyl acetate may have thrown out the original substances which happen to be in solution in a stoichiometric composition. In view of this observation, the formation of this complex has been studied by conductometric method.

Fig. 1 records the curves representing the conductometric titrations of trimethylbenzylammonium chloride (I) and triethylbenzylammonium chloride (II) with zirconium tetrachloride in thionyl chloride solutions. The addition of zirconium tetrachloride solution in thionyl chloride to that of trimethylbenzylammonium chloride (I) lowers the conductance of the latter and, simultaneously, appearance of a white turbidity is observed. Further addition of the acid solution brings about an increase in the amount of the precipitate of the complex, and as a consequence, the conductance records a further fall which continues up to the break represented by the acid/base molar ratio

of 1 : 2. This point indicates the completion of the reaction, maximum of precipitation and minimum of conductance. The decrease in the value of conductance with the formation of normal complex is due to removal of the more mobile chloride ions which combine with thionylium ions provided by the acid solution to form solvent molecules. The course of the reaction may be represented as :

$$2(CH_3)_3N^+.C_7H_7 + 2SOCl^+ + ZrCl_6^{2-} + 2Cl^- \rightarrow [(CH_3)_3N.C_7H_7]_2ZrCl_6 + 2SOCl_2.$$

FIG. 1



1. $ZrCl_4$ against trimethylbenzylammonium chloride
2. „ „ triethylbenzylammonium chloride

Any further addition of the acid solution increases the conductance of the solution which is due to the increase brought in the concentration of thionylium ions. This may be either effected by the dissolution of the normal complex to form acid complex $[(CH_3)_3N.C_7H_7](SOCl)ZrCl_6$ and its subsequent ionisation, or by the ionised solvo-acid which is being added to the reaction mixture. However, the precipitate does not dissolve completely and there is no indication as to the existence of the acid complex.

The titration of triethylbenzylammonium chloride (II) and zirconium tetrachloride in thionyl chloride records similar changes in conductance when the acid solution is added to that of the ansolvo-base in thionyl chloride. Of course, the only conspicuous difference in this titration is the complete solubility of the normal complex. During the course of this titration, the solution remains clear and decrease in conductance is explained as due to the removal of more mobile chloride ions which are taken up by thionylium ions, added to the solution, to form undissociated solvent

molecules. The conductance of the normal complex is expressed by the break at acid/base molar ratio of 1 : 2. Here the formation of normal complex is complete and, any further addition of the acid solution increases the conductance of the solution. Again, there is no indication as to the existence of the acid complex because of the continued increase of conductance without any break at acid/base molar ratio of 1 :1. It is quite clear from these curves that break as to the formation of normal complex occurs at a much high value of conductance when the normal complex is soluble. This difference in the value of conductance at these breaks is ascribed to the ionisation of the complex, which is more soluble in thionyl chloride.

The solutions of stannic chloride in thionyl chloride react with that of tetramethylammonium chloride, trimethylphenylammonium chloride, trimethylbenzylammonium chloride and dimethylphenylbenzylammonium chloride in thionyl chloride to yield normal complexes when equivalent amounts of the reactants are employed. Of course, the solutions of stannic chloride and triethylbenzylammonium chloride in thionyl chloride react to yield a clear solution. Dry ethyl acetate was employed to precipitate out the normal complex from the reaction mixture, and prior to analysis the traces of the solvents were removed under vacuum. The formation of these complexes of stannic chloride in thionyl chloride may be illustrated by interpreting the course of reaction of dimethylphenylbenzylammonium chloride and stannic chloride in thionyl chloride as :

$$[(CH_3)_2N.C_6H_5.C_7H_7]Cl \rightleftharpoons (CH_3)_2N^+.C_6H_5.C_7H_7 + \bar{Cl}$$

$$2(CH_3)_2N^+.C_6H_5.C_7H_7 + 2SOCl^+ + SnCl_6^{2-} + 2Cl^- \rightarrow [(CH_3)_2N.C_6H_5.C_7H_7]_2SnCl_6 + 2SOCl_2.$$

The precipitation of the normal complex helps the equilibrium to shift towards completion of the reaction.

TABLE I

Complex.	M.P.	Colour.	%Metal.		%Chlorine.		%Nitrogen.	
			Found.	Calc.	Found.	Calc.	Found.	Calc.
$[(CH_3)_4N]_2TiCl_6$	310°(d)*	Pale yellow	11.96	11.73	52.00	52.08	6.92	6.85
$[(CH_3)_3N.C_6H_5]_2TiCl_6$	165°(d)	Do	9.33	9.01	39.99	39.96	5.45	5.25
$[(CH_3)_3N.C_7H_7]_2TiCl_6$	183°(d)	Yellow	8.77	8.55	37.21	37.96	4.85	4.99
$[(CH_3)_2N.C_6H_5.C_7H_7]_2TiCl_6$	175°(d)	Greenish yellow	7.08	7.01	31.41	31.10	4.56	4.08
$[(C_2H_5)_3N.C_7H_7]_2TiCl_6$	125°	Dirty yellow	7.25	7.44	33.36	33.72	4.28	4.34
$[(CH_3)_4N]_2ZrCl_6$	322°(d)*	Dirty white	20.59	20.13	46.62	47.13	6.07	6.19
$[(CH_3)_3N.C_6H_5]_2ZrCl_6$	285°(d)	White	16.56	16.80	36.95	36.98	4.69	4.86
$[(CH_3)_3N.C_7H_7]_2ZrCl_6$	225°(d)	Do	14.84	15.07	34.87	35.27	4.53	4.63
$[(CH_3)_2N.C_6H_5.C_7H_7]_2ZrCl_6$	217°(d)	Do	12.55	12.50	29.24	29.26	4.03	3.85
$[(C_2H_5)_3N.C_7H_7]_2ZrCl_6$	175°(d)	Do	13.20	13.22	30.80	30.96	4.09	4.07
$[(CH_3)_4N]_2SnCl_6$	320°(d)*	Do	24.36	24.75	44.01	44.41	6.10	5.83
$[(CH_3)_3N.C_6H_5]_2SnCl_6$	250°(d)	Do	20.01	19.65	35.36	35.27	4.89	4.64
$[(CH_3)_3N.C_7H_7]_2SnCl_6$	265°(d)	Do	18.36	18.78	33.45	33.70	4.56	4.43
$[(CH_3)_2N.C_6H_5.C_7H_7]_2SnCl_6$	212°(d)	Do	15.68	15.70	27.81	28.18	3.70	3.71
$[(C_2H_5)_3N.C_7H_7]_2SnCl_6$	200°	Do	16.70	16.59	30.05	29.77	4.17	3.91

* These compounds decompose without melting while others form coloured liquids on melting.

EXPERIMENTAL

Thionyl chloride (commercial grade) was distilled and the fraction boiling at 74-76° was collected. This sample was then treated with 2% quinoline and refractionated in an all-glass apparatus equipped with a vacuum jacketed fractionating column to provide a liquid of b.p. 75.5°/732mm.

For use in acid-base reactions, this liquid was further refractionated in an all-glass assembly and the fraction at take-off ratio of 1 :10 was collected. This liquid was transferred to reaction tubes equipped with standard joint glass-stoppers under pressure by dry nitrogen to avoid its contact with atmospheric air.

Zirconium tetrachloride, supplied by Johnson Matthey and Co. Ltd., London, was used without any further treatment, while stannic chloride and titanium tetrachloride were redistilled over tin pieces (A.R.) and copper turnings respectively in an all-glass apparatus. The fractions boiling at 112.5-113°/743mm and 130°/745mm respectively were collected. All the quaternary ammonium chlorides employed in these investigations were crystallised from usual solvents before use and the purity was checked by chemical analysis.

The general procedure for the preparation of these complexes consisted in reacting quantities of the tetrachloride and quaternary ammonium chloride in a molar ratio of 1 : 2 in thionyl chloride and solutions of these substances were prepared in a minimum quantity of the solvent. During the preparation of all these complexes care was taken to add acid solutions to that of base in thionyl chloride just to avoid contamination of any acid complex, which may otherwise be formed. The reaction mixture was allowed to stand in an ice-bath for about 45 minutes so as to complete the reaction. Filtration of the precipitate was carried in a sintered glass funnel kept in a special assembly which avoided contact of moisture. All these materials were kept under vacuum before analysis so that occluded solvents should be completely removed. Dry ethyl acetate was employed to precipitate out the complexes of triethylbenzylammonium chloride which were highly soluble in thionyl chloride.

Titanium, zirconium and tin were weighed as dioxides while chlorine was estimated by Volhard's method. The analysis of nitrogen was carried by Drs. Weiler and Strauss of Oxford. The melting points of these complexes are uncorrected.

Conductometric titrations were carried by using precision measuring Bridge Type WBR, No. 108 with logarithmic indicator amplifier Type TAV, IKc No. .034, manufactured by Wissenschaftlich Technische Werkstatten Wielheium/Oby., Germany.

CHEMISTRY DEPARTMENT,
PUNJAB UNIVERSITY,
HOSHIARPUR.

Received March 30, 1960.

[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

OCCURRENCE OF AURAPTENE, UMBELLIFERONE, MARMIN, LUPEOL AND SKIMMIANINE IN THE ROOT OF *AEGLE MARMELOS* CORREA

BY MRS. A. CHATTERJEE AND B. CHAUDHURY

From the root of *Aegle marmelos* Correâ lupeol, skimmianine and three benzo-α-pyrone derivatives, viz., auraptene (geranylumbelliferone), marmin [7- (3: 7-dihydroxy-3: 7-dimethyloctyloxy)-coumarin] and umbelliferone, have been isolated. This is the first isolation of auraptene in this plant.

From the root of *Aegle marmelos* (Fam. Rutaceæ), a well-known medicinal plant of India, auraptene (geranylumbelliferone), marmin [7-(3:7-dihydroxy-3:7-dimethyloctyloxy)-coumarin], umbelliferone, skimmianine [(2,3-b)-4:7:8-trimethoxyfuroquinoline] and a triterpenoid alcohol, lupeol, have been isolated in good yields. The occurrence of these crystalline compounds, excepting auraptene and lupeol, has been observed earlier in the stem-bark of this plant (Chatterjee *et al.*, *J. Amer. Chem. Soc.*, 1949, **71**, 606; *Naturwiss.*, 1955, **42**, 512; *J. Chem. Soc.*, 1959, 1922) but in poor yields. Of all these products, the yield of marmin in the root has been found to be remarkably high (*vide infra*). The various parts of this plant, viz., fruits (Dikshit and Dutta, this *Journal*, 1930, **7**, 579; Späth *et al.*, *Ber.*, 1937, **70**, 1021; Chatterjee and Saha, this *Journal*, 1957, **34**, 228), leaves (Chatterjee and Bose, this *Journal*, 1952, **29**, 425; Chatterjee and Roy, *Science & Culture*, 1957, **23**, 106; Chakravarty and Das Gupta, this *Journal*, 1958, **35**, 194; *J. Chem. Soc.*, 1958, 1580; Chatterjee, Bose and Srimani, *J. Org. Chem.*, 1959, **24**, 687), stem-bark (Mookerjee, *Curr. Sci.*, 1943, **12**, 209; Chakravarty, this *Journal*, 1944, **21**, 401; Chatterjee *et al.*, *loc. cit.*) and heart-wood (Chaterjee and Roy, this *Journal*, 1959, **36**, 267) have been examined chemically, but not the root. The present report is concerned with the results of our investigations on the root of *A. marmelos*.

Ether extract of the plant materials, collected locally, was separated into hydrochloric acid-soluble portion (A), alkali-soluble fraction (B) and a neutral component (C). The portion (C) on concentration and keeping in a refrigerator for a week deposited marmin, $C_{19}H_{26}O_5$, m.p. 124°. The mother-liquor left after removal of marmin (from C) on chromatography over alumina furnished auraptene (geranylumbelliferone), m.p. 71-72° and a triterpenoid alcohol, m.p. 212°, showing the positive Liebermann-Burchard reaction (pink). The latter has been proved to be identical with lupeol ($C_{30}H_{50}O$) by mixed m.p. determination with an authentic sample, by comparison of their spectral measurements, specific rotation data and mixed chromatogram. A further quantity of marmin was obtained from the column by washing it with ethyl acetate.

The basic fraction (A) yielded an alkaloid, m.p. 176°, identified as skimmianine [(2, 3-b)-4:7:8-trimethoxyfuroquinoline] by its analyses and mixed m.p. (undepressed) determination with an authentic sample of the alkaloid. The portion (B) on acidification with hydrochloric acid (*p*H 4-5) yielded umbelliferone, $C_9H_6O_3$. The yields of the above compounds in the root and stem-bark are shown below.

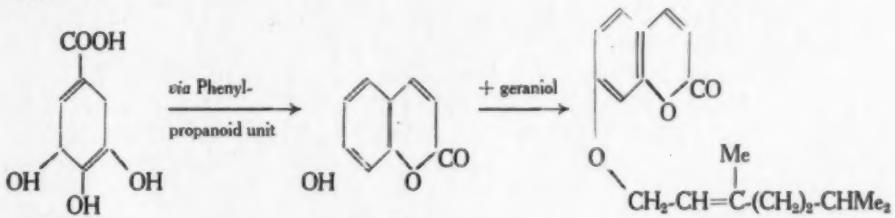
TABLE I

Constituents.	% Yield from	
	Root.	Stem-bark.
Marmin	1.1	0.08
Umbelliferone	0.1	0.02
Skimmianine	0.1	0.0003
Lupeol	0.0058	Nil
Auraptene	0.0028	Nil

The co-occurrence of chemically related compounds, viz., auraptene, marmin and umbelliferone, in the same plant suggests the following pathway of their biogenesis in the plant cells.

The phenylpropanoid unit (C_6-C_3) arising from shikimic acid *via* prephenic acid and phenylalanine (Birch, *Fort. der Chemie org. Naturstoffe*, 1957, **14**, 186) is considered to be the logical precursor of coumarins in Nature. The propanoid unit so formed gives rise to *trans*-cinnamic acid which in turn is transformed into *o*-coumaric acid. The latter is then converted into coumarin. Haworth (*J. Chem. Soc.*, 1942, 448) postulated that *p*-hydroxycinnamic acid is the progenitor of umbelliferone. The support of this hypothesis that coumarins originate from *trans*-cinnamic acid derivatives has been available only recently from the findings of Brown (*Canad. J. Biochem. & Physiol.*, 1955, **33**, 948) and of Kosuge and Conn (*J. Biol. Chem.*, 1959, **234**, 2133). The latter investigators have further demonstrated that shikimic acid is the precursor of *trans*-cinnamic acid.

Based on these findings, the present authors have undertaken the synthesis of marmin (*via* auraptene) under physiological conditions. Umbelliferone, originated from shikimic acid, as stated above, on condensation with geraniol under physiological conditions produces traces of auraptene.



Shikimic acid. (I) Umbelliferone. (II) Auraptene. (III)

Marmin is supposed to arise from auraptene by the action of peroxidase and reductase. Work in this line is being pursued.

EXPERIMENTAL

Isolation of Marmin.—Dried and powdered root of *A. marmelos* Correâ (1.38 kg.) was extracted with petroleum ether (b.p. 40-60°) for 20 hrs. (P). The refuge left after extraction with petroleum ether was soxhletted with ether for another 23 hrs. The ether extract (Q) was reduced to 350 c.c. when a solid (0.25g., m.p. 120-22°) separated. It was collected and washed with the same solvent. The mother-liquor of (Q) was digested with 4*N*-HCl (4×100 c.c.) when a basic portion (A) completely passed into the acid layer. The ether layer was subsequently treated with aqueous KOH (2.5%; 3 × 100 c.c.) to remove phenolic components (B). The neutral ether solution was combined with the petroleum ether (b.p. 40-60°) extract (P; *vide supra*), washed with water, dried over anhydrous powdered sodium sulphate and concentrated to a small bulk (50 c.c.). The latter deposited crystals on keeping in the refrigerator for a week. The crystalline mass, m.p. 120-22°, was collected in a suction and washed with a mixture of ethyl acetate-ether (1:7; 12.04 g.). On several crystallisations from ethyl acetate it formed colorless rods, m.p. 124°, and was identified as marmin from its elementary analyses, rotation and mixed m.p. determination with an authentic sample of the coumarin, isolated in this laboratory (Chatterjee *et al.*, *loc. cit.*, 1959). (Found: C, 68.6; H, 7.5; active H,+ 0.76; C.Me, 4.6; M.W., 325. Calc. for $C_{19}H_{26}O_5$: C, 68.3; H, 7.8; C.Me, 4.5%; M.W., 334). $[\alpha]_D^{30°}$ + 26.°85 (in alcohol).

Reduction of Marmin.—Marmin (0.5 g.) on reduction with $LiAlH_4$ (0.285 g.) in dry tetrahydrofuran (30 c.c.) furnished umbelliferone, in poor yield, and an oil with a terpene-like odour, which could not be identified.

Isolation of Auraptene and Lupeol.—The mother-liquor of (C), left after the removal of marmin, was subjected to chromatographic resolution over neutral alumina, elution having been carried out with benzene and with ethyl acetate.

TABLE II

Eluents.	Fractions.	Residue on evaporation.
Benzene	1-2	Oily mass crystallised from methanol, m.p. 71-72°.
,,	3-9	Solid, m.p. 146-81°.
Ethyl acetate	10-17	Solid melting at a range 109-23°. Crystallised from ethyl acetate, m.p. 120-22°.

The first two fractions furnished auraptene in 0.0028% yield. It was crystallised from methanol, m.p. 71-72°. (Found : C, 76.35; H, 7.64. $C_{19}H_{22}O_3$ requires C, 76.5; H, 7.4%). Lupeol appeared in the latter fractions of benzene eluents. It was crystallised from ethyl acetate, m.p. 212°; $[\alpha]_D^{25°} + 27°.9$ (in chloroform). (Found : C, 84.75; H, 11.52. Calc. for $C_{30}H_{50}O$: C, 84.5; H, 11.7%.) It gave a pink coloration with the Liebermann-Burchard reagent (yield 0.0058%). Ethyl acetate fraction afforded marmin (1.07g.) which on recrystallisation from ethyl acetate yielded colorless crystals, m.p. 124°.

Isolation of Skimmianine.—The acid-soluble portion (A) was basified with sodium carbonate (*p*H 7.5-8) and exhaustively extracted with ether. The ether extract was washed with water and dried over anhydrous sodium sulphate for 2 hrs. Solid (1.2g.) separated after the removal of the solvent was crystallised from ethyl acetate, m.p. 176°. (Found : C, 65.0; H, 5.1; N, 5.30; OMe, 36.1. Calc. for $C_{14}H_{13}O_4N$: C, 64.9; H, 5.0 ; N, 5.4 ; OMe, 35.9%).

Isolation of Umbelliferone.—Alkaline portion (B) was acidified (*p*H 3) with HCl (conc.), kept overnight and extracted with ether. The extract was washed with water and dried over anhydrous sodium sulphate. This on concentration gave an oily mass which was subjected to vacuum sublimation at 155-65°/0.01 mm. It was crystallised from ethanol, m.p. 232°. (Found : C, 66.78; H, 3.86. Calc. for $C_9H_6O_3$: C, 66.67; H, 3.70%).

The authors express their deep appreciation to Mr. W. Manser, E.T.H., Zürich, Switzerland for microanalyses.

DEPARTMENT OF PURE CHEMISTRY,
UNIVERSITY COLLEGE OF SCIENCE,
CALCUTTA-9.

Received December 12, 1959.

[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

DEPENDENCE OF OPTICAL ACTIVITY ON CHEMICAL CONSTITUTION. PART I. SALTS OF ACETIC, PROPIONIC, BUTYRIC, PHENYLACETIC, β-PHENYLPROPIONIC AND CINNAMIC ACIDS WITH CINCHONIDINE

BY MAGHAR SINGH MANHAS AND KALI KUMAR SHUKLA

Cinchonidine salts of acetic, propionic, butyric, phenylacetic, β-phenylpropionic and cinnamic acids have been prepared. The rotatory disperson of the above has been examined in methanol, ethanol, chloroform and pyridine. The effect of solvent and some constitutional factors like homologous series, unsaturation and the presence of a phenyl group on the rotatory power has also been explored.

In view of the conflicting results obtained by earlier investigators on the rotatory powers, using several varieties of optically active compounds (Frankland, *J. Chem. Soc.*, 1912, **101,** 654; 1899, **75,** 347; 1893, **63,** 511, 1410; Hilditch, *ibid.*, 1909, **95,** 1581; Rupe, *Annalen*, 1909, **369,** 311; Singh, *Proc. Ind. Acad. Sci.*, 1949, **30A,** 87, *et seq*), the present authors have selected alkaloids of the cinchona family to provide the asymmetric centre in all the optically active compounds of this series and have undertaken a study of their optical properties.

The present work includes the preparation of cinchonidine salts of acetic, propionic, butyric, phenylacetic, β-phenylpropionic and cinnamic acids. The rotatory dispersion of these salts in different solvents has been studied. The work also incorporates the study of the effect of constitutional factors like homologous series, unsaturation and the presence of phenyl group on the rotatory power of optically active compounds.

EXPERIMENTAL

The cinchonidine salts of different acids were prepared by dissolving equimolecular proportions of the alkaloid and the acid separately and then mixing the two solutions together. The salts separating after cooling and scratching were then repeatedly crystallised from ethanol or mixtures of organic solvents as white needles. These salts are freely soluble in chloroform and pyridine, less so in methanol and ethanol, sparingly soluble in ethyl acetate and acetone and practically insoluble in non-polar solvents. The purity of these compounds was tested by their elementary analysis.

TABLE I

No.	Cinchonidine salts.	M.P.	% Nitrogen. Found.	Calc.
1.	Acetate	.. 125°	8.13	7.91
2.	Propionate	.. 140°	7.84	7.61
3.	Butyrate	.. 85-87°	7.18	7.33
4.	Phenylacetate	.. 144°	6.23	6.51
5.	β-Phenylpropionate	.. 142°	6.56	6.31
6.	Cinnamate	.. 157°	6.28	6.33

The rotatory power determinations were carried out in the visible region of the spectrum for eleven wave-lengths in a 2 dcm polarimeter tube at room temperature (30°). The results are recorded in Tables II to VII.

TABLE II

Cinchonidine acetate.

Solvent :		Pyridine	EtOH	MeOH	$CHCl_3$
Conc. (g./100 c.c.) :		0.5000	0.5000	0.5000	0.5000
Calc.	$[\alpha]$ ..	$\frac{11.33}{\lambda^2 - 0.0640}$	$\frac{21.10}{\lambda^2 - 0.0834}$	$\frac{29.53}{\lambda^2 - 0.0519}$	$\frac{35.57}{\lambda^2 - 0.0353}$
	λ_0 ..	0.2530	0.2888	0.2278	0.1879
Lines.		Obs. [α].	Obs. [α].	Obs. [α].	Obs. [α].
Li_{6708}		−29.00°	−58.00°	−74.00°	−86.00°
Cd_{6438}		32.00	64.00	82.00	94.00
Li_{6104}		37.00	72.00	92.00	105.00
Na_{5893}		40.00	80.00	100.00	114.00
Hg_{5780}		42.00	84.00	104.00	119.00
Hg_{5461}		48.00	98.00	120.00	136.00
Cd_{5085}		58.00	120.00	142.00	159.00
Cd_{4799}		68.00	144.00	166.0	182.00
Cd_{4678}		73.00	156.00	176.00	194.00
Li_{4602}		77.00	164.00	184.00	201.00
Hg_{4358}		90.00	198.00	214.00	230.00

TABLE III

Cinchonidine propionate.

Solvent :		Pyridine	EtOH	MeOH	$CHCl_3$
Conc. (g./100 c.c.) :		0.5000	0.5000	0.5000	0.5000
Calc.	$[\alpha]$ ..	$\frac{10.60}{\lambda^2 - 0.1169}$	$\frac{27.83}{\lambda^2 - 0.0542}$	$\frac{34.98}{\lambda^2 - 0.0233}$	$\frac{37.00}{\lambda^2 - 0.0389}$
	λ_0 ..	0.3420	0.2328	0.1526	0.1972
Lines.		Obs. [α].	Obs. [α].	Obs. [α].	Obs. [α].
Li_{6708}		−32.00°	−70.00°	−82.00°	−90.00°
Cd_{6438}		35.00	77.00	89.00	98.00
Li_{6104}		41.00	87.00	100.00	110.00
Na_{5893}		46.00	95.00	108.00	120.00
Hg_{5780}		48.00	99.00	112.00	125.00
Hg_{5461}		58.00	114.00	127.00	142.00
Cd_{5085}		75.00	136.00	148.00	168.00
Cd_{4799}		93.00	158.00	169.00	193.00
Cd_{4678}		104.00	169.00	179.00	205.00
Li_{4602}		112.00	177.00	185.00	214.00
Hg_{4358}		145.00	205.00	210.00	245.00

TABLE IV

Cinchonidine butyrate.

Solvent :		Pyridine	EtOH	$CHCl_3$	MeOH
Conc. (g./100c.c.) :		0.5000	0.5000	0.5000	0.5000
Calc.	$[\alpha]$ ..	$\frac{13.27}{\lambda^2-0.1015}$	$\frac{31.93}{\lambda^2-0.0342}$	$\frac{38.79}{\lambda^2-0.0441}$	$\frac{39.90}{\lambda^2-0.0202}$
	λ_0 ..	0.3187	0.1849	0.2100	0.1421
Lines.		Obs. [α].	Obs. [α].	Obs. [α].	Obs. [α].
Li_{6708}		−38.00°	−77.00°	−95.00°	−93.00°
Cd_{6438}		42.00	83.00	105.00	101.00
Li_{6104}		49.00	94.00	118.00	113.00
Na_{5893}		54.00	102.00	128.00	122.00
Hg_{5780}		57.00	106.00	134.00	127.00
Hg_{5461}		68.00	121.00	152.00	143.00
Cd_{5085}		84.00	142.00	181.00	167.00
Cd_{4799}		103.00	163.00	208.00	190.00
Cd_{4678}		113.00	173.00	222.00	201.00
Li_{4602}		120.00	180.00	233.00	208.00
Hg_{4358}		150.00	205.00	266.00	235.00

TABLE V

Cinchonidine phenylacetate.

Solvent :		Pyridine	EtOH	MeOH	$CHCl_3$
Conc. (g./100 c.c.) :		0.5000	0.5000	0.5000	0.5000
Calc.	$[\alpha]$ ..	$\frac{7.32}{\lambda^2-0.1038}$	$\frac{22.20}{\lambda^2-0.0712}$	$\frac{28.95}{\lambda^2-0.0487}$	$\frac{32.09}{\lambda^2-0.0326}$
	λ_0 ..	0.3221	0.2263	0.2207	0.1806
Lines.		Obs. [α].	Obs. [α].	Obs. [α].	Obs. [α].
Li_{6708}		−22.00°	−56.00°	−72.00°	−77.00°
Cd_{6438}		24.00	61.00	80.00	84.00
Li_{6104}		27.00	69.00	90.00	94.00
Na_{5893}		30.00	75.00	97.00	102.00
Hg_{5780}		32.00	78.00	101.00	106.00
Hg_{5461}		37.00	90.00	116.00	121.00
Cd_{5085}		47.00	107.00	138.00	142.00
Cd_{4799}		58.00	124.00	150.00	162.00
Cd_{4678}		63.00	132.00	170.00	172.00
Li_{4602}		68.00	138.00	177.00	189.00
Hg_{4358}		85.00	160.00	205.00	204.00

TABLE VI

Cinchonidine β-phenylpropionate.

Solvent :		Pyridine	EtOH	MeOH	$CHCl_3$
Conc. (g./100 c.c.) :		0.2500	0.2500	0.2500	0.2500
Calc.	$[\alpha]$ ..	$\frac{4.948}{\lambda^2 - 0.1239}$	$\frac{18.54}{\lambda^2 - 0.0575}$	$\frac{25.95}{\lambda^2 - 0.0589}$	$\frac{29.41}{\lambda^2 - 0.0531}$
	λ_0 ..	0.3520	0.2398	0.2427	0.2304
Lines.		Obs. [α].	Obs. [α].	Obs. [α].	Obs. [α].
Li_{6708}		− 15.00°	− 48.00°	− 66.00°	− 74.00°
Cd_{6438}		17.00	52.00	74.00	81.00
Li_{6104}		20.00	58.00	82.00	92.00
Na_{5893}		22.00	64.00	90.00	100.00
Hg_{5780}		24.00	68.00	94.00	105.00
Hg_{5461}		28.00	78.00	108.00	120.00
Hg_{5085}		36.00	92.00	130.00	143.00
Cd_{4799}		46.00	108.00	152.00	166.00
Cd_{4678}		52.00	114.00	162.00	177.00
Li_{4602}		56.00	120.00	170.00	185.00
Hg_{4358}		75.00	140.00	198.00	215.00

TABLE VII

Cinchonidine cinnamate.

Solvent :		Pyridine	EtOH	MeOH	$CHCl_3$
Conc. (g./100 c.c.) :		0.5000	0.2500	0.2500	0.2500
Calc.	$[\alpha]$ ..	$\frac{8.10}{\lambda^2 - 0.1225}$	$\frac{26.43}{\lambda^2 - 0.0326}$	$\frac{35.05}{\lambda^2 - 0.0551}$	$\frac{37.69}{\lambda^2 - 0.0572}$
	λ_0 ..	0.3500	0.1805	0.2347	0.2392
Lines.		Obs. [α].	Obs. [α].	Obs. [α].	Obs. [α].
Li_{6708}		− 25.00°	− 64.00°	− 88.00°	− 96.00°
Cd_{6438}		28.00	70.00	98.00	106.00
Li_{6104}		32.00	78.00	110.00	120.00
Na_{5893}		36.00	84.00	120.00	130.00
Hg_{5780}		38.00	88.00	126.00	136.00
Hg_{5461}		46.00	100.00	144.00	156.00
Cd_{5085}		59.00	116.00	172.00	188.00
Cd_{4799}		75.00	134.00	200.00	218.00
Cd_{4678}		84.00	142.00	214.00	234.00
Li_{4602}		91.00	148.00	224.00	244.00
Hg_{4358}		120.00	168.00	260.00	284.00

DISCUSSION

Nature of Rotatory Dispersion.—The dispersion is found to be "simple" as it obeys Drude's one-term equation :

$$[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$$

In this equation K and λ_0 are constants and represent the absolute rotation of the substance and the wave-length of the dominant absorption band of its molecule in the ultraviolet region of the spectrum respectively.

TABLE VIII

‡No.	$[\alpha]^{30}_{5461}$			
	$CHCl_3$ *(5.2)	Pyridine (12.4)	EtOH (25.8)	MeOH (31.2)
1.	−136.0° (37.57)**	−48.00° (11.33)	−98.00° (21.10)	−120.0° (29.53)
2.	142.0 (37.00)	58.00 (10.60)	114.0 (27.83)	127.0 (34.98)
3.	152.0 (38.79)	68.00 (13.27)	121.0 (31.93)	143.0 (39.90)
4.	121.0 (32.09)	37.00 (7.32)	90.00 (22.20)	116.0 (28.95)
5.	120.0 (29.41)	28.00 (4.948)	78.00 (18.54)	108.00 (25.95)
6.	156.0 (37.69)	46.00 (8.10)	100.0 (26.43)	144.0 (35.05)

*The figures in the brackets refer to the dielectric constant of the solvent.
**The figures in the brackets refer to the rotation constant, K.
‡The number of the compounds corresponds to those in Table I.

Effect of Solvent on the Rotatory Power.—From Table VIII it appears that $[\alpha]^{30}_{5461}$ of cinchonidine salts in the four solvents decreases with the corresponding increase in the dielectric constant of the solvent. Chloroform stands out as an exception in all cases.

Rule *et al.* (*J. Chem. Soc.*, 1931, 674, 2652 ; 1932, 1400, 1409, 2332 ; 1933, 376, 1217) undertook an extensive study of the change of optical rotatory power caused by solvents. Whatever regularity in the change of rotations with the change of solvents that could be achieved has been correlated with the dipole moment values of the solvents. However, there are many exceptions and no precise inference can possibly be arrived at.

A reference to the present work indicates that all the salts of cinchonidine show the highest value of rotation in chloroform and lowest in pyridine. The values in methanol and ethanol are intermediate between these two extremes. Almost identical conclusions have been arrived at for the change of rotatory power values of quinine salts in these solvents by Manhas and Banerjee (this *Journal*, 1959, **36,** 865). Therefore it is difficult to attribute the change in the rotatory power values to the dipole moment of the solvents in question only.

Earlier works of Manhas and Banerjee on brucine salts (*Proc. Nat. Acad. Sci., India*, 1957, **26A,** 285 ; *J. Univ. Saugar*, 1957, **6,** 23 ; *Res. Bull. Chem. Soc. Univ. Saugar*, 1958, **1,** 13 ; this *Journal*, 1959, **36,** 669) and a more recent study undertaken by Perti *et al.* (private communication)

on strychnine salts of substituted aromatic acids show that both these series of compounds exhibit the highest rotation in pyridine.

As compounds with similar constitution are found to behave almost analogously in different solvents as regards their rotatory effect, it seems reasonable to conclude that the constitution of the solvent with respect to that of the optically active solute may also have an important bearing in determining its rotatory power.

Effect of Homologous Series.—Hilditch (*loc. cit.*) has studied the menthyl esters of aliphatic dibasic acids and has come to the conclusion that there is a decrease of rotation in passing from the first to the second, and after that an increase up to the fifth member whereas in the case of brucine salts of these acids, the value goes on increasing up to the third and from there decreases *via* fourth up to the fifth member of the series.

Frankland (*loc. cit.*) in reviewing the work of earlier investigators states that in ascending series of optically active esters of amyl alcohol and menthol with aliphatic monobasic acids, the values of molecular rotation increase with the molecular weight of the compound up to the third or fourth member of the series and then attain almost a constant value.

Evidently Hilditch's results are at variance with Frankland's observations and, hence, it seems desirable to further study the change of rotatory power in ascending a homologous series.

Table IX records the values of $[M]_{5461}^{30°}$, the molecular rotatory power, of the salts of cinchonidine with acetic, propionic and butyric acids in different solvents.

TABLE IX

Cinchonidine salts.	$[M]_{5461}^{30°}$			
	$CHCl_3$.	Pyridine.	EtOH.	MeOH.
Acetate	—481.4°	—169.5°	—346.9°	—424.8°
Propionate	522.5	213.4	419.5	467.3
Butyrate	580.6	259.7	462.2	546.3

A comparison of these values shows that as molecular weight of the compound in this homologous series increases, there is a gradual enhancement in the molecular rotation. These results are in agreement with Frankland's observations where a similar increase in the rotatory power has been noted.

Effect of Phenyl Group.—Frankland (*J. Chem. Soc.*, 1893, **63,** 511, 1410; 1899, **75,** 347) has further stated that the molecular rotation in homologous series increases to an approximately constant value on ascending the series, but this rule does not hold good if an aromatic group is situated at some distance from the asymmetric carbon atom. Phenyl group in close proximity to the optically active part of the molecule exercises a disturbing influence on the latter, but the variation depends entirely on the relative position of the aromatic group, and almost disappears if the group is not in the immediate neighbourhood of the asymmetric atom.

Rupe and Wolfsleben (*Annalen*, 1913, **395,** 136) discussing the optical rotatory power of several esters of *d*-carvoxime conclude that the entrance of a phenyl group into acetic acid or phenylacetic acid or the replacement of methyl by phenyl in acetic acid or crotonic acid diminishes the rotatory power of carvoxime; the entrance of phenyl into α and β positions in cinnamic acid increases the rotatory power. Just the reverse behaviour is observed with the menthyl esters of the acids.

It appears from this work that the replacement of hydrogen atom by a phenyl group in an optically active compound produces a change in the rotatory power. However, it is difficult to say whether this type of change in the constitution of the molecule will lead to an enhancement of rotation or its lowering.

TABLE X

Cinchonidine salts.	$[M]_{5461}^{30°}$			
	$CHCl_3$.	Pyridine.	EtOH.	MeOH.
Acetate	−481.4°	−169.9°	−346.9°	−424.8°
Phenylacetate	520.3	159.1	387.0	499.0
Propionate	522.5	213.4	419.5	467.3
β-Phenylpropionate	532.8	124.3	346.3	479.5

The results of such measurements by the authors on some of the cinchonidine salts are recorded in Table X. It will be observed that with the exception of pyridine, the values of $[M]_{5461}^{30°}$ are higher for cinchonidine phenylacetate than for the acetate salt in all the solvents. However, the comparison of the values of molecular rotation of the propionate and β-phenylpropionate shows that the phenyl salt has higher values in chloroform and methanol whereas in pyridine and ethanol the values are lower than the corresponding values of the propionate. These results also indicate that introduction of the phenyl group does not produce a uniform change in the molecular rotatory power of the asymmetric molecule.

However, a comparison of the values of $[\alpha]_{5461}^{30°}$ shows that the introduction of the phenyl group in place of hydrogen atom leads to a lowering of the rotation values in all cases and in all solvents (Table VIII).

Effect of Unsaturation.—The general consensus of opinion is that the introduction of unsaturation introduces an irregularity in the rotatory power and, in general, the unsaturated linkage leads to a higher rotation.

Pickard and Kenyon (*J. Chem. Soc.*, 1911, **99,** 45) while comparing the molecular rotatory powers of the esters and salts of phenylpropionic acid and cinnamic acid have also come to the same conclusion. This is supported by the work of later investigators also.

TABLE XI

Cinchonidine salts.	$[M]_{5461}^{30°}$			
	$CHCl_3$.	Pyridine.	EtOH.	MeOH.
β-Phenylpropionate	−532.8°	−124.3°	−346.3°	−479.5°
Cinnamate	689.5	203.3	442.0	636.5

The observations of the authors recorded in Table XI show that the molecular rotation of cinchonidine cinnamate is greater in all solvents under examination than that of the β-phenylpropionate. This indicates that the conversion of a saturated to an ethylenic linking is accompained by an enhancement in the rotatory power. This is in agreement with observations of earlier workers like Rupe (*Annalen*, 1903, **327,** 157; *Ber.*, 1903, **36,** 27, 2796), Pickard and Kenyon (*loc cit.*) and Singh (*J. Chem. Soc.*, 1920, **117,** 1599).

The authors are grateful to the University of Saugar for providing research facilities and to Dr. O. N. Perti, Head of the Department of Chemistry, Th. D.S.B., Govt. College, Nainital, for making available his manuscript material on strychnine salts.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SAUGAR,
SAUGAR (M.P.)

Received March 4, 1960.

[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

COMPOUNDS OF CADMIUM BROMIDE AND IODIDE WITH AMINES AND HETEROCYCLIC BASES

By Sarju Prasad, K. S. R. Krishnaiah and T. Ranganathachar

Compounds of cadmium bromide and iodide with primary (mono and di) and secondary amines and heterocyclic bases have been prepared in ethanol, their properties studied and structures discussed.

Compounds of cadmium halides with urea (Neubauer and Kerner, *Annalen*, 1875, **101**, 337), with 3 :5-dibromo-*o*-toluidine (Hann and Spencer, *J. Wash. Acad. Sci.*, 1925, **15**, 163), with ethylenediamine (Grossmann and Schück, *Z. anorg. Chem.*, 1906, **50**, 21), with chloro- and bromo-benzylquinolines (Mikailenko, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 2253), with *o*-phenylenediamine and *o*-toluylenediamine (Wahl, Forh III Nord. Kemistmotete, 1928, pp. 172-176) and with dodecylamine (Broome *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 67) have been previously reported in literature.

The present investigation was undertaken with a view to studying the formation of the compounds of $CdBr_2$ and CdI_2 with amines and heterocyclic bases in absolute ethanol medium.

Experimental

The amines, heterocyclic bases, $CdBr_2$ and CdI_2 used were of Merck's or B.D.H. 'extra pure' quality. Ethanol was distilled over lime and redistilled over anhydrous copper sulphate.

An ethanolic solution of the amine or heterocyclic base was added to $CdBr_2$ or CdI_2 solution in ethanol with constant stirring till the precipitation was complete. The precipitate was filtered, and washed with absolute alcohol till the washings did not form any precipitate with the corresponding cadmium halide solution. It was dried at about 100° in an air-oven, analysed and properties studied.

Bromine or iodine was estimated by Piria and Schiff's method, and cadmium as cadmium sulphate. Nitrogen was estimated by Kjeldahl's method in a few cases, and for the rest, it was obtained by difference. In the case of compounds of $CdBr_2$ with primary monoamines and secondary amines, the amine was estimated potentiometrically by bromate-bromide mixture and the percentage of nitrogen in the compound calculated.

Table I

Compounds of cadmium iodide with primary mono- and diamines.

Amine.	Compound formed.	M.P.	% Cadmium.		% Iodine.		% Amine.	
			Found.	Calc.	Found.	Calc.	Found.	Calc.
1. Aniline	$Cd(C_6H_5NH_2)_2\ I_2$	182°	20.17	20.35	45.81	45.96	34.02	33.69
2. α-Naphthylamine	$Cd(C_{10}H_7NH_2)_2\ I_2$	207°	17.36	17.23	39.20	38.90	43.44	43.87
3. β-Naphthylamine	Do	196°	17.10	17.23	38.82	38.90	44.08	43.87
4. *o*-Toluidine	$Cd(CH_3.C_6H_4.NH_2)_2\ I_2$	167°	19.29	19.36	43.48	43.73	37.23	36.91
5. *m*-Toluidine	Do	178°	19.23	19.36	43.46	43.73	37.12	36.91
6. *p*-Toluidine	Do	184°	19.22	19.36	43.60	43.73	37.18	36.91
7. Benzylamine	$Cd(C_6H_5.CH_2NH_2)_2\ I_2$	Decompose before melting	19.45	19.36	43.60	43.73	36.95	36.91
8. Benzidine	$Cd(NH_2.C_6H_4\text{-}C_6H_4.NH_2)\ I_2$	Do	20.37	20.42	45.78	46.13	33.85	33.45
9. *p*-Phenylenediamine	$Cd\left\{C_6H_4(NH_2)_2\right\}\ I_2$	Do	23.48	23.69	53.22	53.51	23.30	22.80

TABLE II

Compounds of cadmium bromide with amines and heterocyclic bases.

	Amine or heterocyclic bases.	Compound formed.	% Cadmium. Found.	% Cadmium. Calc.	% Bromine. Found.	% Bromine. Calc.	% Nitrogen, Found.	% Nitrogen, Calc.
1.	Aniline	$Cd(C_6H_5NH_2)_2\ Br_2$	24.50	24.56	34.81	34.87	6.098	6.108
2.	α-Naphthylamine	$Cd(C_{10}H_7NH_2)_2\ Br_2$	20.17	20.14	28.48	28.63	5.041	5.017
3.	β-Naphthylamine	Do	20.09	20.14	28.60	28.63	4.992	5.017
4.	o-Toluidine	$Cd(CH_3.C_6H_4.NH_2)_2\ Br_2$	23.03	23.13	32.63	32.87	5.742	5.757
5.	m-Toluidine	Do	23.09	23.13	32.76	32.87	5.740	5.757
6.	p-Toluidine	Do	23.21	23.13	32.69	32.87	5.776	5.757
7.	o-Anisidine	$Cd(CH_3O.C_6H_4NH_2)_2\ Br_2$	21.85	21.69	30.67	30.84	5.364	5.403
8.	p-Anisidine	Do	21.81	21.69	30.73	30.84	5.388	5.403
9.	o-Phenetidine	$Cd(C_2H_5O.C_6H_4.NH_2)_2\ Br_2$	20.47	20.57	29.09	29.25	5.109	5.128
10.	p-Phenetidine	Do	20.71	20.57	29.21	29.25	5.117	5.128
11.	Benzylamine	$Cd(C_6H_5.CH_2NH_2)_2\ Br_2$	23.24	23.12	32.75	32.87	5.751	5.759
12.	Benzidine	$Cd(NH_2.C_6H_4-C_6H_4.NH_2)\ Br_2$	24.89	24.63	34.99	35.01	6.081	6.141
13.	o-Tolidine	$Cd(CH_3.NH_2.C_6H_3-C_6H_3.NH_2.-CH_3)\ Br_2$	23.37	23.21	32.86	33.01	5.722	5.784
14.	m-Phenylenediamine	$Cd\left\{C_6H_4(NH_2)_2\right\}\ Br_2$	29.77	29.56	41.94	42.03	7.310	7.365
15.	p-Phenylenediamine	Do	29.59	29.56	41.96	42.03	7.293	7.365
16.	o-Dianisidine	$Cd(CH_3O.NH_2.C_6H_3-C_6H_3.NH_2.-OCH_3)\ Br_2$	21.85	21.77	30.91	30.96	5.392	5.425
17.	Phenylhydrazine	$Cd(C_6H_5NH.NH_2)\ Br_2$	29.68	29.56	41.89	42.03	7.324	7.365
18.	Ethylaniline	$Cd(C_6H_5.NHC_2H_5)_2\ Br_2$	21.83	21.85	30.96	31.08	5.495	5.445
19.	Benzylaniline	$Cd(C_6H_5.NHC_6H_5)_2\ Br_2$	18.49	18.42	26.12	26.19	5.555	5.588
20.	Pyridine	$Cd(C_5H_5N)_2\ Br_2$	26.20	26.12	37.31	37.15	6.468	6.509
21.	α-Picoline	$Cd(C_6H_7N)_2\ Br_2$	24.54	24.56	34.78	34.87	6.124	6.108
22.	γ-Picoline	Do	24.68	24.56	34.81	34.87	6.098	6.108
23.	Piperidine	$Cd(C_5H_{11}N)_2\ Br_2$	25.59	25.42	35.99	36.14	6.327	6.333
24.	Quinoline	$Cd(C_9H_7N)_2\ Br_2$	21.40	21.19	29.95	30.14	5.278	5.281
25.	Piperazine	$Cd(C_4H_{10}N_2)\ Br_2$	31.41	31.37	44.41	44.61	7.872	7.816

DISCUSSION

All the compounds are stable at the room temperature but decompose when treated with strong acids. Excepting the compounds formed with benzidine and o-tolidine, all the rest dissolve in H_2SO_4 (dilute). These decompose into the corresponding amine, sodium bromide and cadmium hydroxide when treated with NaOH (dilute).

$$Cd\ (2\ Am)\ Br_2 + 2\ NaOH \rightarrow Cd\ (OH)_2 + 2\ NaBr + 2\ Am.$$

The compounds formed with diamines are comparatively stable and hydrolyse slowly even on boiling with dilute alkali solution. All these compounds are insoluble in ethanol, benzene and acetone. The compounds formed with primary monoamines are, however, sparingly soluble in acetone.

The compounds of $CdBr_2$ with amines and heterocyclic bases are stable towards heat up to 300°, but decompose above that temperature before melting. The compounds of $CdBr_2$ with α-and β-naphthylamines decompose above 200° before melting. When heated with sodalime, the corresponding amine or heterocyclic base seperates out and condenses on the cooler parts of the test tube.

In all the cases studied, two molecules of a monoamine or a heterocyclic base and one molecule of a diamine attach themselves to one molecule of $CdBr_2$ or CdI_2. The E.A.N. of cadmium assumes inert gas configuration and the compounds are fairly stable.

The authors' sincere thanks are due to the authorities of the Banaras Hindu University for providing necessary facilities.

CHEMICAL LABORATORIES,
BANARAS HINDU UNIVERSITY,
VARANASI-5.

Received January 28, 1960.

[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

COMPLEX COMPOUNDS OF STANNOUS BROMIDE WITH AMINES AND HETEROCYCLIC BASES

By Sarju Prasad, K. S. R. Krishnaiah and V. Hariharan

Compounds of stannous bromide with primary (mono and di) and secondary amines and heterocyclic bases have been prepared in ether medium, their properties studied and structures discussed.

Compounds of stannous halides with ammonia (Biltz and Fischer, *Z. anorg. allgem. Chem.*, 1923, **129,** 1; Sofianopoulis, *Compt. rend.*, 1911, **152,** 865) and methylamine (Everest, *J. Chem. Soc.*, 1952, 1670) have been previously described. Karanthsis (*Bull. Soc. Chim.*, 1926, *iv*, **39,** 43) prepared $SnI_3.NMe_4$ by dissolving molecular proportions of SnI_2 and Me_4NI in the presence of an excess of HCl. By a similar method he prepared the corresponding compounds: $SnI_3.NH_3Ph$ and $SnI_3.NHPh$. Dimitron (*Praktika*, 1929, **4,** 140) isolated the compounds $MeSnI_3.2\ C_5H_5N$, $SnCl_4.2C_9H_7N$ and $SnBr_4.2C_9H_7N$.

It is evident that practically no work has been done on the formation of compounds of $SnBr_2$ with amines and heterocyclic bases. The present investigation was therefore undertaken with a view to studying the preparation and properties of these compounds.

Experimental

The amines and heterocyclic bases used were of Merck's or B.D.H. 'extra pure' quality. Ether was distilled over metallic sodium. Anhydrous $SnBr_2$ was prepared by passing dry HBr gas on molten tin and extracted with ether.

A dilute ether solution of the amine or heterocyclic base was added to $SnBr_2$ solution in ether with constant stirring till complete precipitation. The precipitate was filtered and washed with anhydrous ether till the washings did not form any precipitate with $SnBr_2$ solution. It was dried at the room temperature, analysed, and its properties studied.

Bromine was estimated by Piria and Schiff's method and tin as SnO_2. Nitrogen was estimated by Kjeldahl's method in a few cases and for the rest it was obtained by difference. The results are recorded in Table I.

Almost all the compounds are semicrystalline powders insoluble in ether but sparingly soluble in benzene. These are fairly stable in dry atmosphere, but when exposed to moist air these absorb moisture and decompose. These are readily soluble in moderately strong HCl, but decompose into the corresponding amine, sodium bromide and tin hydroxide when treated with dilute NaOH.

$$Sn(2\ Am)\ Br_2 + 2NaOH \rightarrow Sn(OH)_2 + 2\ NaBr + 2Am.$$

When heated, all the compounds decompose before melting excepting the compounds obtained with benzylamine and phenylhydrazine, which melt at 238° and 186° respectively.

TABLE I

Compounds of stannous bromide with amines and heterocyclic bases.

	Bases.	Compound formed.	% Tin Found.	% Tin Calc.	% Bromine. Found.	% Bromine. Calc.	% Nitrogen. Found.	% Nitrogen. Calc.
1.	Aniline	$Sn(C_6H_5NH_2)_2\ Br_2$	25.42	25.58	34.33	34.41	6.042	6.029
2.	α-Naphthylamine	$Sn(C_{10}H_7NH_2)_2\ Br_2$	20.88	21.03	28.18	28.31	4.912	4.961
3.	β-Naphthylamine	Do	21.12	21.03	28.38	28.31	4.953	4.961
4.	o-Toluidine	$Sn(CH_3.C_6H_4.NH_2)_2\ Br_2$	24.21	24.11	32.22	32.44	5.634	5.685
5.	m-Toluidine	Do	23.98	24.11	32.26	32.44	5.646	5.685
6.	p-Toluidine	Do	24.18	24.11	32.18	32.44	5.672	5.685
7.	o-Anisidine	$Sn(CH_3O.C_6H_4.NH_2)_2\ Br_2$	22.48	22.62	30.42	30.45	5.342	5.335
8.	m-Anisidine	Do	22.71	22.62	30.31	30.45	5.352	5.335
9.	p-Anisidine	Do	22.57	22.62	30.38	30.45	5.328	5.335
10.	o-Phenetidine	$Sn(C_2H_5O.C_6H_4.NH_2)_2\ Br_2$	21.39	21.47	28.88	28.91	5.042	5.065
11.	p-Phenetidine	Do	21.51	21.47	28.97	28.91	5.102	5.065
12.	Benzylamine	$Sn(C_6H_5.CH_2NH_2)_2\ Br_2$	24.02	24.11	32.38	32.44	5.691	5.685
13.	Benzidine	$Sn(NH_2C_6H_4\text{-}C_6H_4NH_2)\ Br_2$	25.72	25.67	34.42	34.56	6.098	6.056
14.	o-Tolidine	$Sn(CH_3.NH_2.C_6H_3\text{-}C_6H_3.NH_2.\text{-}CH_3)\ Br_2$	24.28	24.20	32.43	32.58	5.682	5.710
15.	o-Phenylenediamine	$Sn\{C_6H_4(NH_2)_2\}Br_2$	30.74	30.71	41.10	41.33	7.228	7.244
16.	m-Phenylenediamine	Do	30.82	30.71	41.23	41.33	7.316	7.244
17.	p-Phenylenediamine	Do	30.62	30.71	41.27	41.33	7.287	7.244
18.	o-Dianisidine	$Sn(CH_3O.NH_2.C_6H_3\text{-}C_6H_3.NH_2.\text{-}OCH_3)\ Br_2$	22.60	22.72	30.52	30.58	5.351	5.359
19.	Phenylhydrazine	$Sn(C_6H_5NH.NH_2)\ Br_2$	30.83	30.71	41.30	41.33	7.304	7.244
20.	Methylaniline	$Sn(C_6H_5.NHCH_3)_2\ Br_2$	24.20	24.11	32.18	32.44	5.672	5.685
21.	Ethylaniline	$Sn(C_6H_5.NHC_2H_5)_2\ Br_2$	22.74	22.81	30.60	30.70	5.368	5.380
22.	Pyridine	$Sn(C_5H_5N)_2\ Br_2$	27.16	27.19	36.40	36.60	6.459	6.415
23.	Piperidine	$Sn(C_5H_{11}N)_2\ Br_2$	26.53	26.46	35.48	35.62	6.223	6.243
24.	Piperazine	$Sn(C_4H_{10}N_2)\ Br_2$	32.60	32.57	43.56	43.83	7.762	7.683

DISCUSSION

In all the cases studied, two molecules of a monoamine or a heterocyclic base and one molecule of a diamine attach themselves to one molecule of $SnBr_2$ and only the covalency of four is attained. It appears that amines or heterocyclic bases attach themselves to the central atom, chelete compounds being formed in the case of diamines and can be represented as $Sn(2Am)Br_2$ (where A= monoamine or heterocyclic base) and $Sn(D)Br_2$ (where D=diamine). The E.A.N. does not assume the inert gas configuration and therefore the compounds are not very stable.

The authors' sincere thanks are due to the authorities of the Banaras Hindu University for providing the necessary facilities.

CHEMICAL LABORATORIES,
BANARAS HINDU UNIVERSITY,
VARANASI-5.

Received January 28, 1960.

[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

THE APPARENT DISSOCIATION CONSTANTS OF DIETHYLDITHIOCARBAMIC ACID

By K. P. Soni and A. M. Trivedi

Soduim diethyldithiocarbamate is found to be a diacidic base, diethyldithiocarbamic acid being an ampholyte. The values of the two acidic dissociation constants, as found out by Bjerrum's method, by E.M.F. measurements, are: $pk_1 = 7.5$ (-SH group) and $pk_2 = 8.4$ [$-NH^+(C_2H_5)_2$].

Sodium diethyldithiocarbamate is a well-known reagent for the colorimetric estimation of copper (Callan and Henderson, *Analyst*, 1929, **54,** 650; Hoar, *ibid.*, 1937, **62,** 657). The corresponding acid is unstable and has not been isolated (Heilbron and Bunbury, "Dictionary of Organic Compounds," published by Eyre and Spottiswoode, 1953, Vol. II, p. 184). According to Martin (*Anal. Chem.*, 1953, **25,** 1260), the acid is unstable at *p*H 1 to 3. The dissociation constant of the acid has been found polarographically to be of the order of 10^{-7} (Sartori and Calzolari, *Chem. Abs.*, 1952, **46,** 6968). Its value is found polarographically in 60% ethanol to be 2.9×10^{-6} (Gregg and Tyler, *J. Amer. Chem. Soc.*, 1950, **72,** 4561).

Experimental

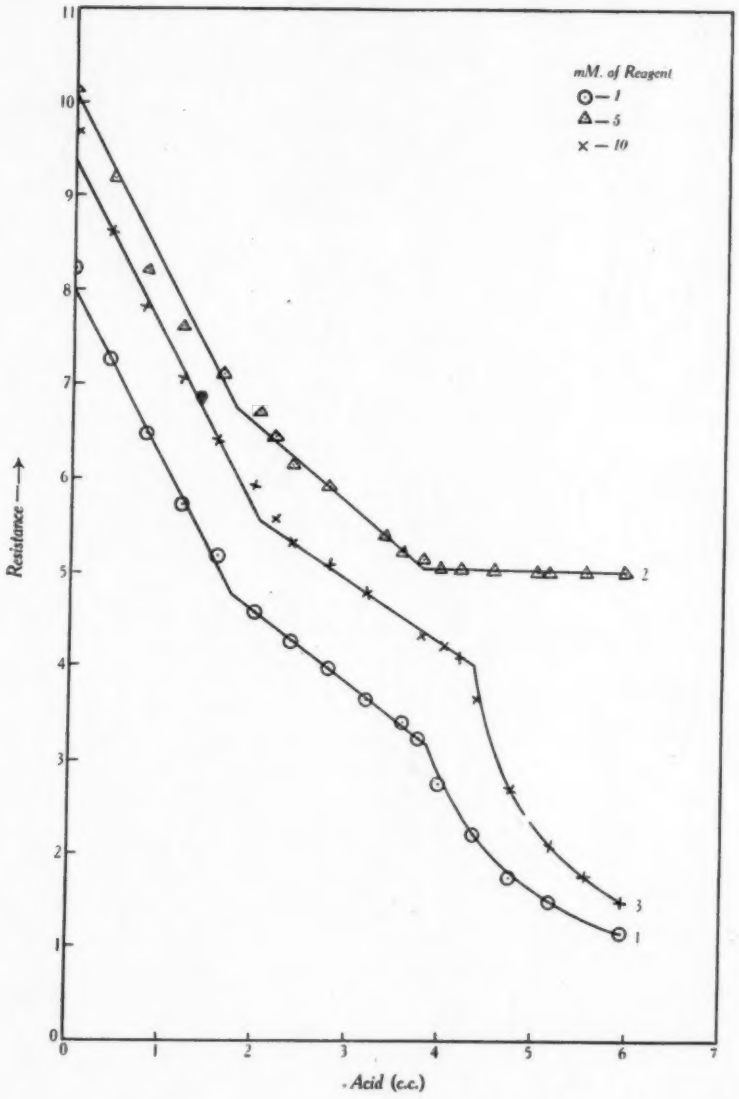
Conductometric and *p*H methods were employed for the investigation. The sodium salt was of A.R. quality of B.D.H. company. All other chemicals used were either A.R. or similar quality. Conductivity measurements were made at $35° \pm 0.1°$, employing the Leeds and Northrup assembly. *p*H measurements were made at 30° by a Beckman *p*H meter, model H-2. Suitable buffers were employed to standardise the *p*H meter. Solutions of 1, 2, 5 and 10 m*M*/litre of the substance were prepared by direct weighing and titrated against standard acids of suitable concentration either conductometrically or by *p*H measurements. Solutions of 25 or 50 c.c. aliquots were employed and different amounts of acid added. It was found that there was a continuous shift in the observations which became steady only after 24 hours. Hence, a uniform procedure was adopted in which aliquot solutions with different amounts of acid added were kept at room temperature for 24 hours before measurements were made.

Conductivity Measurement

Suitable aliquots (25 or 50 c.c.) of 1, 2, 5 and 10 milimolar solutions of the sodium salt were titrated against perchloric, hydrochloric and acetic acids of suitable normalities. The typical curve of

each of the acids is shown in Fig. 1, curves 1–3. The resistances were corrected for the volume change. The curves are drawn of resistances against c.c. of titrant added.

FIG. 1



Curve No.	Scale-axis.		Reagent.		Acid used.	End-point.	
	X 1 unit = c.c.	Y 1 unit = ohms.	mM.	c.c. taken.		Required.	Obtained.
1	1	250	1	50	0.02633 *N*-HCl	3.80	3.80
2	0.5	50	5	50	0.2550 *N*-HAc	1.96	2.00
3	1	25	10	50	0.2340 *N*-$HClO_4$	4.27	4.30

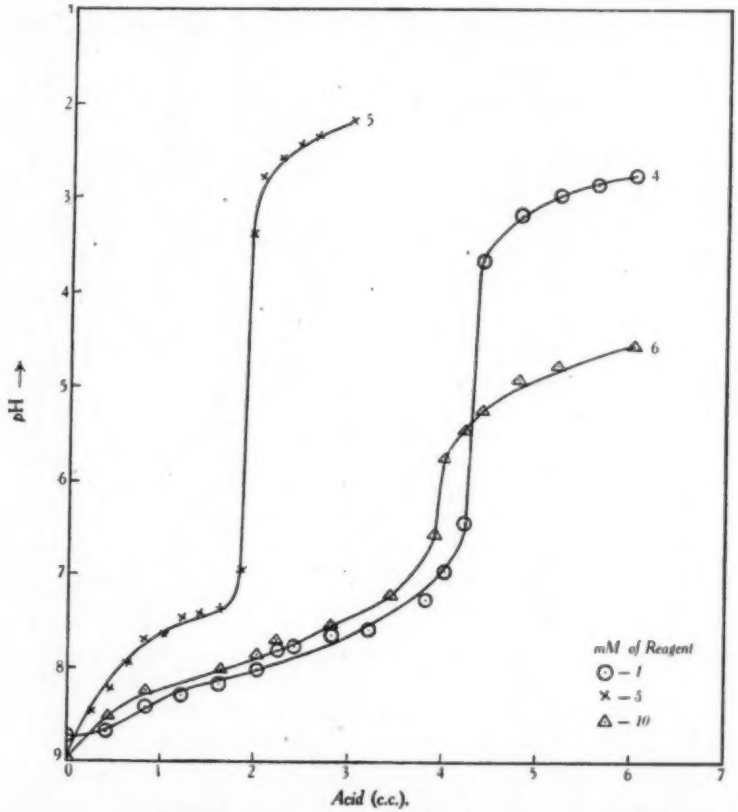
*p*H *Measurement*

The above solutions were also utilised for *p*H measurements. The conductometric titrations show that the corresponding acid formed is a dibasic one. This has also been confirmed by this method. The end-point was obtained when nearly double the equivalents of the titrant acid was added. Some typical observations and three curves, one with each acid, are recorded in Table I and in Fig. 2 (curves 4–6).

TABLE I

Acid.	Normality.	*m*M of Na-salt.	pk_1.	pk_2.
HCl	0.00884	1	7.4	8.5
HCl	0.0884	10	7.5	8.7
HCl	0.1050	2	7.7	8.6
HCl	0.1050	5	7.4	8.4
$HClO_4$	0.0234	1	7.5	8.3
$HClO_4$	0.2340	10	7.4	8.2
CH_3COOH	0.2550	5	7.7	8.4
CH_3COOH	0.2550	10	7.5	8.3

FIG. 2.



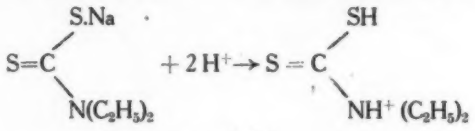
Curve No.	Reagent. *m*M.	Reagent. c.c. taken.	Acid used.	End-point. Required.	End-point. Obtained.
4	1	50	0.02340*N*-$HClO_4$	4.27	4.30
5	5	50	0.2633*N*-HCl	1.90	1.90
6	10	50	0.2550*N*-HAc	3.92	3.90

DISCUSSION

Both *p*H and conductometric measurements have shown that sodium diethyldithiocarbamate is a diacidic base. This has not been apparently reported before. We shall first consider the E.M.F. data. When 50 c.c. of 0.005*M* of the sodium salt is neutralised by 0.2633*N*-HCl, sharp inflection is obtained on addition of 1.90 c.c. of the acid (Fig. 2, curve 5). This gives the normality of the sodium salt 0.01, [(0.2633×1.9)/50] ; since molarity of the salt is 0.005, it is obvious that the salt is diacidic. In Fig. 2 (curves 4–6) the *X*-axis represents c.c. of 0.02340*N*-$HClO_4$, 0.2633*N*-HCl, and 0.2550*N*-CH_3COOH, added to 50 c.c. of 1, 5, and 10 m*M* of the sodium salt respectively. If instead of c.c., equivalents of the acids added were plotted, the graphs would have clearly shown that in each case a sharp inflection had occurred when two equivalents of the acids were added. However, present method of graphical representation appears preferable, as in the latter case all the three curves will fall almost on the same line before neutralisation.

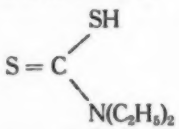
Similarly, a careful consideration of the conductivity data reveals the same point, *i.e.*, two equivalents of the acid are required for complete neutralisation. 50 c.c. of 0.001*M* sodium salt requires 3.80 c.c. of 0.02633*N*-HCl (Fig. 1, curve 1), when a sharp inflection is observed. On the other hand, it has been observed that when one equivalent of the acid is added, the inflection point is not predominant. This is due to pk_1 and pk_2 differing by about one unit only.

pk_1 and pk_2 have been determined, following Bjerrum's method (Bjerrum, "Metal Ammine Formation in Aqueous Solution", P. Haase and Son, Copenhagen, 1941). According to Bjerrum, pk_1 and pk_2 are obtained when the acid is 1/4 and 3/4 neutralised respectively. The values of pk_1 and pk_2 are shown in Table I. The sodium salt on treating with acid changes its conductance or *p*H slowly and becomes ultimately diacidic. This change may be represented as:



(I)

Diethyldithiocarbamic acid may be represented as:



The behaviour of this acid may be compared with those of ampholytes. In this case-SH is an acidic group and $-NEt_2$ is a basic one. The conjugate acid of the basic group will be $-NH^+Et_2$. Therefore two acidic groups, dissociation constants of which are found out in the present case, will be -SH and $-NH^+(C_2H_5)_2$, and the corresponding dibasic acid will be as represented by (I). By analogy with tertiary aliphatic amines, $NH^+(C_2H_5)_2$ may be considered to be a weaker acidic group (pk_2=8.4) and -SH may be considered to be the stronger one (pk_1=7.5).

Thanks are due to the Ahmedabad Education Society and the Gujarat University, for a grant towards chemicals and apparatus.

DEPARTMENT OF CHEMISTRY,
M. G. SCIENCE INSTITUTE,
AHMEDABAD-9.

Received November 30, 1959.

[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

THIAZOLIDONES. PART IV. SYNTHESIS OF 2-ARYL-3-BENZYL-4-THIAZOLIDONES

By B. K. Raval and J. J. Trivedi

Schiff's bases from aryl aldehydes and benzylamines have been condensed with thioglycollic acid to obtain 2-aryl-3-benzyl-4-thiazolidones.

2-Aryl-3-alkyl-4-thiazolidones exhibit anticonvulsant and anaesthetic properties (Troutman and Long, *J. Amer. Chem. Soc.*, 1948, **70,** 3436; Surrey, *ibid.*, 1949, **71,** 3354; Chen *et al.*, *Arch. Neurol. Psychiat.*, 1951, **66,** 329). In the light of anticonvulsant properties shown by *N*-benzyl-β-chloropropionamide (Kushner *et al.*, *J. Org. Chem.*, 1951, **16,** 1283), it was considered of interest to prepare 2:3-disubstituted thiazolidones having a benzyl group. With this end in view, several 2-aryl-3-substituted benzyl-4-thiazolidones have now been prepared by the condensation of Schiff's bases (not isolated) from aryl aldehydes and benzylamines with thioglycollic acid.

Experimental

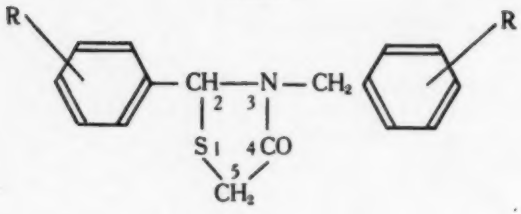
2-Aryl-3-benzyl-4-thiazolidones were synthesised by the procedure adopted by Surrey *et al.* (*J. Amer. Chem. Soc.*, 1947, **69,** 2911) with slight modifications.

A mixture of aldehyde (0.02 *M*) and benzylamine (0.02 *M*) in dry benzene (25 c.c.) was refluxed with a Dean and Stark water separator. After the theoretical quantity of water had separated (4-5 hours), thioglycollic acid (2.0 g.) was added and refluxing was continued till water had ceased to separate.

Thiazolidones from benzaldehyde and substituted benzylamines separated directly from benzene solution. In other cases, the residue, after removal of benzene, was taken up in ether, washed successively with sodium bicarbonate solution, dilute HCl (1:1) and 10% sodium bisulphite solution to remove respectively any acid formed during the reaction, benzylamine and aldehyde, remaining unchanged. It was finally washed with water, dried over anhydrous sodium sulphate and the solvent evaporated. The oily residue deposited crystals on long standing (in some cases a month).

Thiazolidones (yields about 60%) were crystallised from ethanol. Compounds are listed in Table I.

TABLE I



No.	R = .	R' = .	M.P.	Formula.	% Sulphur. Found.	Calc.
1.	H	H	153-54°	(Troutman & Long, *loc. cit.*)		
2.	H	*o*-Cl	122°	$C_{16}H_{14}ONClS$	10.7	10.5
3.	H	*p*-Cl	154°	,,	10.4	,,
4.	H	*m*-CH_3	98°	$C_{17}H_{17}ONS$	11.1	11.3
5.	H	*p*-CH_3	130°	,,	11.4	,,
6.	H	3:4-DiMe	126°	$C_{18}H_{19}ONS$	10.9	10.8
7.	H	2:4-DiMe	156°	,,	11.0	,,
8.	H	2:5-DiMe	82°	,,	10.6	,,
9.	H	*p*-Br	147°	$C_{16}H_{14}ONBrS$	9.0	9.2
10.	H	*p*-OCH_3	138°	$C_{17}H_{17}O_2NS$	10.9	10.7
11.	*o*-Cl	H	75°	$C_{16}H_{14}ONClS$	10.4	10.5
12.	*o*-Cl	*o*-Cl	110°	$C_{16}H_{13}ONCl_2S$	9.7	9.5
13.	*o*-Cl	*p*-Br	103°	$C_{16}H_{13}ONClBrS$	8.5	8.4
14.	*p*-Cl	H	73°	$C_{16}H_{14}ONClS$	10.4	10.5
15.	*p*-Cl	*m*-CH_3	115°	$C_{17}H_{16}ONClS$	10.0	10.1
16.	*o*-OH	H	150°	$C_{16}H_{15}O_2NS$	11.1	11.2
17.	*p*-OCH_3	H	62°	$C_{17}H_{17}O_2NS$	10.6	10.7
18.	*p*-OCH_3	3:4-DiMe	86°	$C_{19}H_{21}O_2NS$	9.6	9.8
19.	*p*-OCH_3	2:4-DiMe	112°	,,	10.0	,,
20.	*p*-OCH_3	*p*-Br	119°	$C_{17}H_{16}O_2NBrS$	8.7	8.5

The authors thank Dr. R. D. Desai for interest in the work and the Ahmedabad Education Society for defraying the expenses incurred during the course of this investigation and the Government of India for a research grant to one of them (J.J.T).

CHEMISTRY DEPARTMENT,
M. G. SCIENCE INSTITUTE,
AHMEDABAD-9.

Received January 19, 1960

[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

THIAZOLINYLHYDRAZONES. PART I. SYNTHESIS OF 4-OXO-5-(ARYL)-Δ^2-THIAZOLIN-2-YLHYDRAZONES

By P. R. Pathan, B. K. Raval and J. J. Trivedi

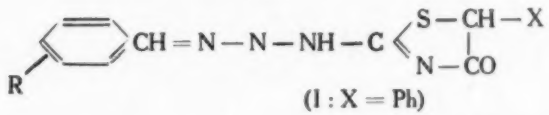
α-Halo-arylacetic acids have been condensed with aryl thiosemicarbazones to obtain the 4-oxo-5-(aryl)-Δ^2-thiazolin-2-ylhydrazones.

Buu Hoï *et al.* (*J. Org. Chem.*, 1956, **21**, 415 ; *J. Chem. Soc.*, 1956, 716) found 4-oxo-Δ^2-thiazolin-2-ylhydrazones to exhibit tuberculostatic activity. Similar compounds with an aryl group on C_5 of the hetero ring do not seem to have been studied. It seemed desirable therefore to prepare thiazolinylhydrazones having an aryl group on C_5 of the hetero ring. α-Bromophenyl- and α-bromo-(*o*-chloro)-phenylacetic acids have been condensed with aryl thiosemicarbazones to yield 4-oxo-5-(phenyl/*o*-chlorophenyl)-Δ^2-thiazolin-2-ylhydrazones.

Experimental

Thiosemicarbazones were prepared from aromatic aldehydes and thiosemicarbazide by the procedure of Buu Hoï *et al.* (*loc. cit.*). α-Bromoarylacetic acids were condensed with aryl thiosemicarbazones as described by Buu Hoï *et al.* (*loc. cit.*). The hydrazones were obtained in 40 to 80% yield and were crystallised from acetic acid.

Table I



(I : X = Ph)

	R=	M.P.	Formula.	% Sulphur. Found.	Calc.
1.	H	260-61°	$C_{16}H_{13}ON_3S$	10.8	10.9
2.	*o*-CH_3	261-62°	$C_{17}H_{15}ON_3S$	10.3	10.4
3.	*p*-OCH_3	266°	$C_{17}H_{15}O_2N_3S$	9.7	9.8
4.	*p*-Cl	275°	$C_{16}H_{12}ON_3ClS$	9.6	9.7
5.	2 : 4-Cl_2	232°	$C_{16}H_{11}ON_3Cl_2S$	8.7	8.8
6.	*o*-Cl	254°	$C_{16}H_{12}ON_3ClS$	9.6	9.7
7.	*o*-OCH_3	228-29°	$C_{17}H_{15}O_2N_3S$	9.7	9.8
8.	*p*-OH	320°	$C_{16}H_{13}O_2N_3S$	10.2	10.3
9.	5-Cl-2-OH	289°	$C_{16}H_{12}ON_3Cl_2S$	9.2	9.3
10.	*p*-$(CH_3)_2$-N	277°	$C_{18}H_{18}ON_4S$	9.4	9.5
11.	*o*-OH	287°	$C_{16}H_{13}O_2N_3S$	10.4	10.3

TABLE II

(I: X = *o*-C_6H_4Cl)

	R=	M.P.	Formula.	% Sulphur. Found.	Calc.
1.	H	272°	$C_{16}H_{12}ON_3ClS$	9.6	9.7
2.	*o*-CH_3	286°	$C_{17}H_{14}ON_3ClS$	9.2	9.3
3.	*p*-OCH_3	266°	$C_{17}H_{14}O_2N_3ClS$	8.8	8.9
4.	*p*-Cl	279°	$C_{16}H_{11}ON_3Cl_2S$	8.9	8.8
5.	2 : 4-Cl_2	276°	$C_{16}H_{10}ON_3Cl_3S$	8.1	8.0
6.	*o*-Cl	258°	$C_{16}H_{11}ON_3Cl_2S$	8.7	8.8
7.	*o*-OCH_3	256°	$C_{17}H_{14}O_2N_3ClS$	8.7	8.9
8.	*p*-OH	334°	$C_{16}H_{12}O_2N_3ClS$	9.1	9.2
9.	5-Cl-2-OH	270°	$C_{16}H_{11}O_2N_3Cl_2S$	8.5	8.4
10.	*p*-$(CH_3)_2$-N	290°	$C_{18}H_{17}O_2N_4ClS$	8.7	8.6
11.	*o*-OH	290°	$C_{16}H_{12}O_2N_3ClS$	9.0	9.2

The authors thank Dr. R. D. Desai for interest in the work and the Ahmedabad Education Society for defraying the expenses incurred during the course of this work, and the Government of India for a research grant to one of them (J.J.T.).

CHEMISTRY DEPARTMENT,
M.G. SCIENCE INSTITUTE,
AHMEDABAD-9.

Received February 18, 1960.

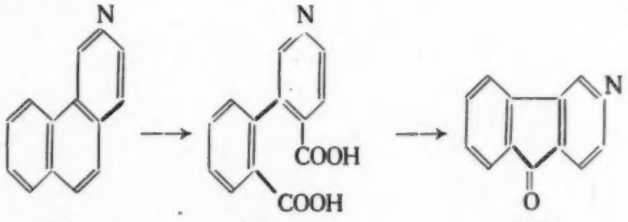
[Jour. Indian Chem. Soc., Vol. **37**, No. 6, 1960]

SYNTHESIS IN THE 3-AZAFLUORENE GROUP. PART II. A NEW SYNTHESIS OF 3-AZAFLUORENONE

By J. N. Chatterjea and K. Prasad

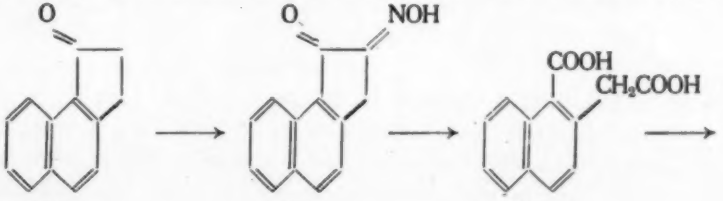
7 : 8-Benzo*iso*quinoline has been unambiguously synthesised and degraded to 3-azafluorenone.

In Part I of this series compounds of the 3-azafluorene group have been reached from difficult accessible pyridine derivatives (Chatterjea and Prasad, *Chem. Ber.*, 1960, **93,** in press). It transpired that compounds of this group should be accessible by degradation of a suitable polynuclear heterocyclic compound (cf. Skraup and Gobenzl, *Monatsh.*, 1883, **4,** 436 ; *Ber.*, 1883, **16,** 2306 ; Ciusa and Buono, *Gazzetta*, 1950, **80,** 864 ; Koelsch and Steinhauer, *J. Org. Chem.*, 1953, **18,** 1516) and for this purpose, 7 :8-benzo*iso*quinoline (I) or its derivatives appeared as attractive intermediates. In fact, (I) was readily oxidised with boiling potassium permanganate to afford 3-*o*-carboxyphenyl-*iso*nicotinic acid (II) which on pyrolysis furnished 3-azafluorenone (III), identical with the specimen obtained before.

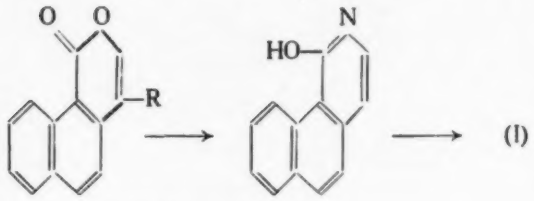


(I) (II) (III)

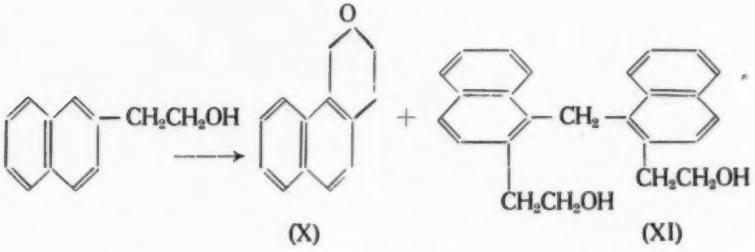
As the synthesis of 7 :8-benzo*iso*quinoline by Koelsch and Lindquist (*J. Org. Chem.*, 1956, **21,** 657) was both laborious and ambiguous, an alternative synthesis was undertaken. 2-Naphthaldehyde, now prepared conveniently by the reduction of 2-naphthonitrile by lithium triethoxyaluminohydride (Brown *et al.*, *Tetrahedron Letters*, 1959, III, 9) was converted into the related acrylic acid by condensation with malonic acid and then reduced and cyclised to the known 6:7-benzoindan-1-one (Cook and Hewett, *J. Chem. Soc.*, 1933, 1098). The 2-*iso*nitroso derivative (V) on the Beckmann rearrangement with *p*-toluenesulphonyl chloride in alkali, followed by hydrolysis, yielded 1-carboxynaphthalene-2-acetic acid (VI). This was followed by esterification with diazomethane, condensation with methyl formate and cyclisation of the resulting hydroxymethylene compound with warm hydrochloric acid to methyl 7 :8-benzo*iso*coumarin-4-carboxylate (VII). This was hydrolysed by hydrochloric acid and decarboxylated to 7 :8-benzo*iso*coumarin (VIII). This on heating with ethanolic ammonia afforded 1-hydroxy-7 :8-benzo*iso*quinoline (IX), also described by Koelsch and Lindquist (*loc. cit.*) by an entirely different method. 7 :8-Benzo*iso*quinoline was obtained from it by reduction of the 1-chloro derivative with palladised charcoal and hydrogen in presence of sodium hydroxide in ethanolic solution (cf. Bailey *et al.*, *J. Chem. Soc.*, 1950, 2277).



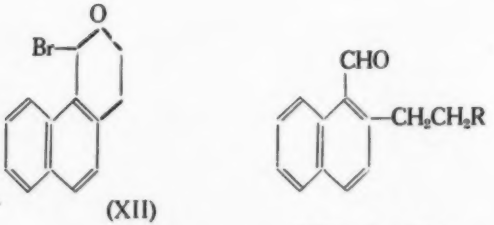
(IV) (V) (VI)



(VII : R = CO_2Me)
(VIII : R = H)



(X) (XI)

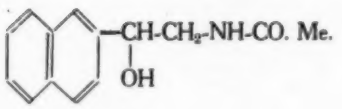


(XII)

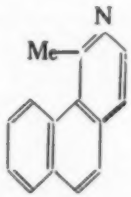
(XIII : R = OH)
(XIV : R = Br)

The recent elegant work of Reihe and Schmitz (*Chem. Ber.*, 1956, **89,** 1254 ; cf. Schmitz, *ibid.*, 1958, **91,** 1133) on the new synthesis of *iso*quinolines prompted us to attempt the synthesis of (I) along the same lines. 2-β-Naphthylethanol, now prepared in excellent yield by reduction of ethyl β-naphthylacetate by lithium aluminium hydride, furnished 7 :8-benzo*iso*chroman (X) in moderate yield on treatment with paraformaldehyde along with di-(β-2-hydroxyethyl-α-naphthyl)methane (XI), characterised as its 3 :5-dinitrobenzoate. Bromination of (X) to the 1-bromo derivative (XIII) was not smooth and led to complex mixtures ; attempts to isolate the rearranged aldehyde (XIV) from the crude product by way of the bisulphite compound was unsuccessful. However, treatment of the crude brominated product with 2 :4-dinitrophenylhydrazine furnished a small quantity of the 2 :4-dinitrophenylhydrazone of (XIII).

During this work, 1-methyl-7 :8-benzo*iso*quinoline (XVI) was also prepared by Pictet-Gam's cyclisation of *N*-acetyl-2-hydroxy-2-(β-naphthyl)ethylamine (XV), now readily obtained by the reduction of ω-acetamido-β-acetonaphthone (Day and Immediata, *J. Org. Chem.*, 1940, **5,** 512) by potassium borohydride. The yield of the *iso*quionoline (XVI) was so poor that further work was not possible.



(XV)



(XVI)

*EXPERIMENTAL

2-Naphthaldehyde.—2-Naphthonitrile (1 *M*) was added to a solution of lithium triethoxyaluminohydride (prepared by careful addition of 1.5*N* ethyl acetate to 1.3*M* lithium aluminium hydride in dry ethereal solution), maintained at -2°. After the addition the mixture was stirred for 3 hours at 0° and the excess of the hydride destroyed by the addition of methanol. The mixture was worked up in the usual manner to afford 2-naphthaldehyde, yield 50% (crude).

6 :7-*Benzoindan*-1-*one.*—A mixture of the crude 2-naphthaldehyde (10 g.), malonic acid (30 g.), piperidine (2 c.c.) and pyridine (50 c.c.) was heated on a water-bath for 6 hours when the reaction was practically over. On working up, β-2-naphthylacrylic acid was obtained, m.p. 195° (Rousset, *Bull. Soc. Chim.*, 1897, **17,** 813, records m.p. 196°), yield 12.2 g.

The acrylic acid (10 g.) was suspended in water and sodium amalgam (400 g., 2.5%) was added in small lots to the warm mixture (40-50°) with stirring. The reaction was considered complete when no more of the acrylic acid separated as the sodium salt on cooling. β-2-Naphthylpropionic acid was obtained on acidification, crystallising from aqueous ethanol in colorless plates, m.p. 135° (Mayer and Sieglitz, *Ber.*, 1922, **55,** 1855, record m.p. 135°), yield 8.9 g.

The propionic acid was cyclised according to Cook and Hewett (*loc. cit.*) by warming with stannic chloride. After decomposition with water, the indanone was extracted from the resulting solid by ether (yield 8 g.). A considerable portion of the compound remained as insoluble *tin complex* from which the ketone was recovered (about 3 g.) by extracting with boiling pyridine. Attempted cyclisation of the propionic acid with trifluoroacetic anhydride gave only a tar even at the room temperature.

The 2 :4-*dinitrophenylhydrazone* crystallised from acetic acid in orange-red needles, m.p. 295° (decomp.). (Found : N, 15.30. $C_{19}H_{14}O_4N_4$ requires N, 15.46%).

2-iso*Nitroso*-6 : 7-*benzoindan*-1-*one.*—The above indanone (8 g.) was dissolved in ethanol (25 c.c.) containing amyl nitrite (15 g.) and warmed on the water-bath. To the stirred solution HCl (conc., 6 c.c.) was added and the stirring continued for 1 hour. The iso*nitroso* derivative, which separated gradually on cooling, was collected and crystallised from ethanol in colorless needles, m.p. 234-35° (decomp.), yield 7.5 g. (Found : N, 6.80. $C_{13}H_9O_2N$ requires N, 6.63%).

1-*Carboxynaphthalene*-2-*acetic Acid.*—A solution of the *iso*nitroso compound (6 g.) in warm 10% NaOH solution (60 c.c.) was gradually treated with stirring with *p*-toluenesulphonyl chloride (8 g.) at 40° and the solution completed by heating the mixture on the water-bath. 10% NaOH solution (40 c.c.) was further added, the mixture refluxed for 4 hours, cooled, acidified and extracted with ether when the *acetic acid* was obtained as sandy prisms, yield 5 g. For analysis, the compound was crystallised from water (charcoal) and obtained in colorless prisms, m.p. 184-85° (gas evolution). (Found : C, 67.23 ; H, 4.60. $C_{12}H_{10}O_4$ requires C, 67.83 ; H, 4.38%).

* All m.p.s. are uncorrected.

The crude acid (4.9 g.) was esterified by treatment with an excess of ethereal diazomethane. The *dimethyl ester* distilled at 184°/2 mm and obtained as a thick viscous liquid, yield 4.12 g. (Found : C, 70.01 ; H, 5.60. $C_{15}H_{14}O_4$ requires C, 69.75 ; H, 5.46%).

7 :8-*Benzoisocoumarin.*—A mixture of the foregoing ester (4 g.) in dry ether (40 c.c.) and methyl formate (5 g.) was added to anhydrous sodium methoxide (from sodium, 0.8 g.), stirred at the room temperature and left overnight. Next day, more methyl formate (3 g.) was added and the mixture refluxed for 1 hour. After removal of the ether, the residue was dissolved in water (12 c.c.) and warmed on the water-bath after addition of acetic acid (5 c.c.) and HCl (conc., 5 c.c.). *Methyl* 7 :8-*benzoisocoumarin-4-carboxylate* separated in fine silky needles, yield 2.9 g. The compound was crystallised from acetic acid in colorless needles, m.p. 157°. (Found : C, 70.63 ; H, 4.18. $C_{15}H_{10}O_4$ requires C, 70.85 ; H, 3.96%).

The ester (2.8 g.) was refluxed with a mixture of acetic acid (6 c.c.) and HCl (conc., 8 c.c.) for 12 hours. This was cooled, diluted with water and the crystalline mass so obtained consisted of a mixture of 7 :8-*benzoisocoumarin* (1.5 g.) and 7 :8-*benzoisocoumarin-4-carboxylic acid* (1.2 g.), separated with the help of sodium bicarbonate. The latter (m.p. of the crude material, 249°) was mixed with copper bronze (0.1 g.) and decarboxylated by heating above the melting point, and then on distillation in vacuum, 7 :8-benzo*iso*coumarin was obtained ; total yield 2.1 g. The *iso*coumarin was crystallised from ethanol as a colorless crystalline mass, m.p. 144°. (Found : C, 79.50 ; H, 4.43. $C_{13}H_8O_2$ requires C, 79.56 ; H, 4.11%).

1-*Hydroxy-7:8-benzoisoquinoline.*—A mixture of the foregoing *iso*coumarin (2.0 g.) and ethonolic ammonia (10 c.c., saturated at 0°) was heated at 140° in a sealed tube for 10 hours. 1-Hydroxy-7:8-benzo*iso*quinoline separated from the alcoholic solution in nearly colorless prismatic needles. It was purified by sublimation in vacuum, m.p. 202° (Koelsch and Lindquist, *loc. cit.*, record m.p. 200-201°). (Found : N, 7.23. Calc. for $C_{13}H_9ON$: N, 7.18%).

7:8-*Benzoisoquinoline.*—The above hydroxy*iso*quinoline was converted into 1-chloro-7 : 8-benzo*iso*quinoline according to Koelsch and Lindquist (*loc. cit.*). This chloro compound (1.2 g.) was dissolved in methanol containing KOH (0.5 g.) and shaken in an atmosphere of hydrogen in the presence of palladised charcoal (0.4 g., 5%). Hydrogenation was complete in 20 minutes. The mixture was filtered and the alcoholic filtrate worked up to furnish 7:8-benzo*iso*quinoline in 0.95 g. yield. The *picrate* was crystallised from butanol in yellow needles, m.p. 232° (Koelsch and Lindquist, *loc. cit.*, record m.p. 216°). (Found : C, 56.00; H, 3.10. Calc. for $C_{13}H_9N.^1$ $C_9H_3O_7N_3$ C, 55.88; H, 2.97%). The *picrolonate* crystallised from butanol in a yellow crystalline mass, m.p. 278-80° (decomp.). (Found : N, 16.09. $C_{13}H_9N.C_{10}H_8O_5N_4$ requires N, 15.79%).

3-o-*Carboxyphenylisonicotinic Acid.*—A mixture of 7:8-benzo*iso*quinoline (0.85 g.) and water (80 c.c.) was boiled under reflux while a saturated solution of $KMnO_4$ (2.2 g.) in water was added during 30 minutes. Oxidation was rapid and complete. The mixture was filtered, residual manganese dioxide washed with water and the filtrate concentrated to a small bulk (5 c.c.) and acidified with acetic acid, when the diabasic *acid* separated as colorless leaflets, m.p. 265° (decomp), yield 0.5 g. *U V spectrum* : End on absorption in ethanol. (Found : N, 5.34. $C_{13}H_9O_4N$ requires: N, 5.76%).

3-*Azafluorenone.*—The above dicarboxylic acid (0.45 g.) was pyrolysed at about 360° (metal bath) for 10 minutes in a test tube. The whole was extracted with hot benzene and filtered through an alumina column; the yellow band which was eluted with benzene was collected. 3-*Azafluorenone* was extracted from the benzene solution by HCl (dilute), the acid extract made alkaline and

extracted with ether. On removal of the ether, 3-azafluorenone was obtained as lemon-yellow crystals, crystallising from a small volume of ethanol in yellow plates, m.p. 128-29°, undepressed on admixture with the specimen obtained earlier (Part I, *loc. cit.*), yield 15 mg.

β-2-*Naphthylethanol.*—A solution of ethyl 2-naphthylacetate (30 g.) in ether (50 c.c.) was cautiously added to a slurry of $LiAlH_4$ (10 g.) in ether (100 c.c.). The addition was maintained at such a rate so as to keep the ether boiling. After the addition the mixture was refluxed for ½ hour and the excess of the hydride destroyed by the addition of ethyl acetate and finally with HCl (dilute). The ethereal solution was separated, dried with anhydrous magnesium sulphate and the residue after removal of the ether was distilled in vacuum. β-2-Naphthylethanol was obtained as a colorless solid, m.p. 70-71° (Sontag, *Compt. rend.*, 1933, **197,** 1130, records m.p. 65-68°), yield 23 g.

7:8-*Benzoisochroman.*—A mixture of β-2-naphthylethanol (22 g.), paraformaldehyde (5.5 g.) in dry carbon disulphide (125 c.c.), cooled in a freezing mixture, was saturated with dry hydrogen chloride with mechanical stirring. There was an immediate separation of a crystalline solid which gradually went into solution. The passage of hydrogen chloride was continued for 8 hours and the mixture left overnight at the room temperature. Next day, the mixture was treated with ice-cold water, organic layer removed, dried and the solvent distilled. The residual liquid was heated at 100° in vacuum (30 mm) for 3 hours and then distilled under reduced pressure. 7:8-*Benzoisochroman* was obtained as a colorless mobile liquid, b.p. 150-55°/2.5 mm, solidifying to a colorless crystalline solid, m.p. 38-40° (from petroleum ether), yield 12.5 g. (Found: C, 84.50; H, 6.79. $C_{13}H_{12}O$ requires C, 84.74; H, 6.58%).

The *picrate* was crystallised from ethanol in yellow needles, m.p. 134-35°. (Found: N, 10.12. $C_{13}H_{12}O.C_6H_3O_7N_3$ requires N, 10.17%).

The higher boiling residue distilled at 270-75°/2.5 mm, solidified on keeping and was obtained as colorless plates, m.p. 58°, and was identified as di-(β-2-hydroxyethyl-α-naphthyl)methane (XI), yield 5.1 g. (Found: C, 83.89; H, 6.95. $C_{25}H_{24}O_2$ requires C, 84.23; H, 6.79%).

The *di*-3:5-*dinitrobenzoate*, prepared in pyridine, was crystallised from ethanol in nearly colorless crystalline powder, m.p. 174°. (Found: N, 7.91. $C_{35}H_{28}O_{12}N_4$ requires N, 7.52%).

Bromination of 7:8-*benzoisochroman.*—To a solution of the *iso*chroman (10 g.) in dry CCl_4 (10 c.c.) a solution of bromine (8 g.) in the same solvent (10 c.c.) was added in bright sunlight. The addition of bromine produced a turbidity (due to the separation of an intermediate oily compound) which gradually disappeared. When all the bromine had been added, the mixture was irradiated with ultraviolet light and then refluxed on the water-bath for ½ hour. By this time, the deep brown colour of the mixture disappeared, forming a straw-yellow solution. After the removal of the solvent, the residue was heated at 140° under vacuum for one hour and then distilled. The fraction, b.p. 180-90°/2.5 mm, did not afford any bisulphite compound on stirring for several days with a saturated solution of sodium bisulphite. Nevertheless, on prolonged boiling with 2:4-dinitrophenylhydrazine in ethanol containing phosphoric acid, the 2:4-*dinitrophenylhydrazone* of (XIII) was obtained, crystallising from a large volume of acetic acid as orange-red plates, m.p. 274°, yield 0.4 g. (Found: C, 59.35; H, 4.00. $C_{19}H_{16}O_5N_4$ requires C, 59.99; H, 4.24%).

N-*Acetyl*-β-*hydroxy*-β-(2-*naphthyl*)*ethylamine.*—ω-Acetamido-2-acetonaphthone (2.5 g.) (Day and Immediata, *loc. cit.*) was suspended in water (50 c.c.) and stirred vigorously. To this an aqueous solution of potassium borohydride (2.0 g. in 10 c.c. of wtater) was added gradually. Stirring

was continued for 10 hours and the frothing kept under control by the addition of a few drops of ether. After setting the mixture aside overnight, the fine silky needles were collected, washed with ice-cold water, and obtained as silky needles on crystallisation from water, m.p. 95°. (Dey and Rajagopalan, *Chem. Abs.*, 1940, **34**, 5086, record m.p. 96°), yield, 1.2 g.

7:8-*Benzo*-1-*methylisoquinoline*.—The above acetyl compound (0.5 g.) was dissolved in xylene (30 c.c.), treated with phosphoric anhydride (3 g.), boiled and stirred mechanically. Further amounts of phosphoric anhydride (2×3.0 g.) were added at the interval of ½ hour. After heating for 1½ hours, the mixture was cooled and worked up to afford the *isoquinoline* as an oil in a very small quantity. This readily furnished a *picrate*, m.p. 245°, from ethanol. (Found : C, 57.00; H, 3.20; N, 12.95. $C_{14}H_{11}N.C_6H_3O_7N_3$ requires C, 56.87; H, 3.34 ; N, 13.27%).

The authors wish to thank the authorities of the Patna University for a generous grant which partly defrayed the cost of the investigation.

Chemical Laboratory,
Science College, Patna-5.

Received February 18, 1960

[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

CHALKONES. PART III. SYNTHESIS OF METHYLCHALKONES

By Durga Nath Dhar*

Eight new chalkones have been synthesised by the Claisen-Schmidt condensation and their 2:4-dinitrophenylhydrazones have been prepared.

In continuation of the previous work (Dhar and Lal, *J. Org. Chem.*, 1958, **23,** 1159) on chalkones, the present paper records the synthesis of some hitherto-unknown chalkones with different substituents, viz., methyl, methoxy, hydroxy, present either in the styryl or in the phenyl nucleus.

**Experimental

Resacetophenone dimethyl ether (Perkin *et al.*, *J. Chem. Soc.*, 1908, **93,** 1109), *o*-tolylaldehyde (Williams *et al.*, "Org. Syntheses," Coll. Vol. III, 1955, p. 349), and *p*-tolylaldehyde (Coleman and Craig, "Org. Syntheses", Coll. Vol. II, 1943, p. 583) were prepared as described previously. *m*-Tolylaldehyde was prepared from *m*-tolunitrile *via* Stephen's reaction (*J. Chem. Soc.*, 1925, 1874).

2 : 4-Dimethylacetophenone was prepared in 54% yield by a slight modification of the method of Perkin and Stone (*ibid.*, 1925,2283), using aluminium chloride instead of anhydrous ferric chloride. Its 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate in deep orange-red microneedles, m.p. 170-70.5°. (Found : N, 16.91. Calc. for $C_{16}H_{16}O_4N_4$: N, 17.07%).

When wetted with concentrated sulphuric acid the chalkones, described herein, exhibit halochromism—the colour imparted range from orange to deep red. Ferric chloride develops a light brown colour with an ethanolic solution of 2-hydroxy-2′ : 5′-dimethylchalkone, while the isomeric 2-hydroxy-2′ : 4′-dimethylchalkone (I) fails to respond to this test. Furthermore, it is interesting to find that (I) melts to a green liquid, which dissolves in benzene with the production of a violet colour, while the crystalline chalkone, in benzene, forms a pale yellow solution.

2 : 5-Dimethylacetophenone was prepared by the Friedel-Crafts reaction of *p*-xylene with acetyl chloride by the method described by Fleisher and Freund (*Annalen*, 1917, **414,** 5). The 2 : 4-dinitrophenylhydrazone crystallised from ethyl acetate in elongated biconvex plates, m.p. 170-71°, depressed to 150° on admixture with the isomeric 2 : 4-dimethylacetophenone 2 : 4-dinitrophenylhydrazone (m.p. 170-70.5°). (Found : N, 17.05. Calc. for $C_{16}H_{16}O_4N_4$: N, 17.07%).

The synthesis of chalkones was effected according to the procedure of Schraufstätter and Deutsch (*Chem. Ber.*, 1948, **81,** 489). The method consists in the addition of about 50% aqueous KOH to benzaldehyde and acetophenone derivative in ethanol and keeping the mixture at room temperature for several hours as such or heating for a short time on a water-bath. The various chalkones prepared are recorded in Table I and their corresponding 2 : 4-dinitrophenylhydrazones in Table II.

* Present address : Division of Medicinal Chemistry, Central Drug Research Institute Lucknow.

** All melting points are uncorrected.

TABLE I

Chalkone.	Colour & cryst. shape.	Crystallised from.	M.P.	Formula.	% Carbon. Found.	% Carbon. Calc.	% Hydrogen. Found.	% Hydrogen. Calc.
2′:4′-Dimethoxy-4-methyl-	Bright yellow tiny prismatic needles	Ethanol	117°	$C_{18}H_{18}O_3$	76.50	76.63	6.50	6.40
2′-Hydroxy-2-methyl-	Yellow rhombic crystals	,,	83-84°	$C_{16}H_{14}O_2$	80.69	80.67	5.81	5.88
2′-Hydroxy-3-methyl-	Yellow silky needles	,,	64°	$C_{16}H_{14}O_2$	80.81	80.67	5.62	5.88
2′-Hydroxy-4-methyl-	Yellow rectangular plates	,,	117-18°	$C_{16}H_{14}O_2$	80.54	80.67	6.11	5.88
2-Hydroxy-2′:5′-dimethyl-	Yellow clusters of biconvex microplates	Aq. ethanol	120-21°	$C_{17}H_{16}O_2$	80.72	80.95	6.30	6.34
4-Methoxy-2′:5′-dimethyl-	Yellow rectangular plates	Ethanol	85-85.5°	$C_{18}H_{18}O_2$	80.92	81.20	6.54	6.76
2-Hydroxy-2′:4′-dimethyl-	Yellow microneedles	Aq. ethanol	119°	$C_{17}H_{16}O_2$	80.58	80.55	6.25	6.34
4-Methoxy-2′:4′-dimethyl-	Pale yellow rectangular crystals	Ethanol	40-41°	$C_{18}H_{18}O_2$	81.43	81.20	6.57	6.76

TABLE II

Chalkone 2:4-dinitrophenylhydrazone.	Colour & cryst. shape.	Crystallised from.	M.P.	Formula.	% Nitrogen. Found.	% Nitrogen. Calc.
2′-Hydroxy-2-methyl-	Vermilion-coloured long needles	Xylene	224-25°	$C_{22}H_{18}O_5N_4$	13.26	13.39
2′-Hydroxy-3-methyl-	Vermilion-coloured clusters of radiating needles	,,	222-23°	$C_{22}H_{18}O_5N_4$	13.50	13.39
2′-Hydroxy-4-methyl-	Bright red flat microneedles	,,	237°	$C_{22}H_{18}O_5N_4$	13.42	13.39
2-Hydroxy-2′: 5′-dimethyl-	Vermilion-coloured hexagonal crystals	Ethanol-ethyl acetate	233-35°	$C_{23}H_{20}O_5N_4$	12.64	12.96
4-Methoxy-2′: 5′-dimethyl-	Red flat microneedles	Ethyl acetate	181-82°	$C_{24}H_{22}O_5N_4$	12.85	12.55
2-Hydroxy-2′: 4′-dimethyl-	Vermilion-coloured microneedles	,,	239-40°	$C_{23}H_{20}O_5N_4$	12.54	12.96
4-Methoxy-2′: 4′-dimethyl-	Bright red microneedles	Xylene	218°	$C_{24}H_{22}O_5N_4$	12.38	12.55

The author wishes to thank the Government of India, Ministry of Scientific Research & Cultural Affairs, for the award of a senior research scholarship and to Dr. J. B. Lal for his interest in this work.

H. B. TECHNOLOGICAL INSTITUTE,
KANPUR, U.P.

Received March 9, 1960.

[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

ORGANIC PESTICIDES. PART I. PREPARATION OF SOME FLUORO-ARYLOXY FATTY ACIDS AND THEIR MERCURY DERIVATIVES

BY K. C. JOSHI AND S. C. BAHEL

Several fluoro-aryloxy fatty acids and their mercury derivatives have been prepared as a preliminary to evaluation of their pesticidal activity.

The present work has been undertaken with a view to synthesising aromatic fluorine compounds which might act as potential pest control chemicals. Very little work has been done in this field, and the only work reported is by Finger *et al.* (*J. Amer. Chem. Soc.*, 1959, **81**, 94; Illinois State Geological Survey, Circ. 199, 1955). Some of these compounds exhibit a high fungicidal activity against *Aspergillus niger* and have subsequently found use in the treatment of cotton fabrics and wood for prevention of decay.

In this paper, fluoro-aryloxy fatty acids and their mercury derivatives have been prepared as it has earlier been observed by Sen and Joshi that similar unhalogenated compounds are effective as fungicides and plant growth regulators under different conditions of concentration (this *Journal*, 1951, **28**, 333; *J. Sci. Food Agr.*, 1952, **2**, 526). The introduction of fluorine might therefore be presumed to enhance the toxicity of such compounds.

The fluoro-aryloxy fatty acids have been obtained as usual by condensing fluorophenols with halogenated fatty acids in presence of caustic soda solution (*J. Amer. Chem. Soc.*, 1943, **65**, 1555). *o*-Fluorophenol has been obtained from *o*-anisidine by the Balz-Schiemann reaction, while *p*-fluorophenol has been prepared by the same reaction from both *p*-anisidine and *p*-phenetidine due to limited quantities of either in our stock. The fluoro-aryloxy fatty acids have been mercurated by the method described by Friend ("Inorganic Chemistry", Vol. XI, Part I) and by Sen and Joshi (*loc. cit.*), and their mono-mercurated derivatives obtained.

The pesticidal activity of these compounds is under investigation and will be communicated in due course.

EXPERIMENTAL

o-Fluoroanisole was prepared by the method of English, Mead and Niemann (*J. Amer. Chem. Soc.*, 1940, **62**, 350) from *o*-anisidine (141 c.c.), yield 45 g. (53.4%), b.p. 70-75°/30-35 mm. Bennett *et al.* (*ibid.*, 1935, **57**, 1821) report b.p. 157-59°.

o-Fluorophenol—*o*-Fluoroanisole (45 g.) was demethylated as usual and *o*-fluorophenol isolated as a colorless liquid, b.p. 70–80°/30 mm, yield 15 g. Bennett *et al.* (*loc. cit.*) report b.p. 151-52°.

p-Fluorophenetole was prepared similarly from *p*-phenetidine (60 c.c.), yield 36 g., b.p. 75–80°/80–85 mm. Suter *et al.* (*J. Amer. Chem. Soc.*, 1939, **61**, 161) report b.p. 54°/7 mm.

p-Fluoroanisole was obtained from *p*-anisidine (40 g.) by the above method, yield 18 g. (44%), b.p. 155-57°. Adams *et al.* ("Organic Reaction", Vol. V. p. 212) report b.p. 156-57°.

p-Flurophenol.—Both *p*-fluoroanisole (36 g.) and *p*-fluorophenetole (36 g.) were dealkylated as usual, respective yield and b.p. being 16 g. (22%) and 24 g. (28.5%) and 185-86° (Finger *et al.*, *loc. cit.*, report 185°).

α-Bromo-fatty Acids.—α-Bromopropionic and -butyric acids were prepared by heating freshly distilled dry acids with bromine in the presence of PCl_3 (Vogel, "Practical Organic Chemistry", p. 421). Their boiling points correspond to those previously recorded.

Fluoro-aryloxy acids were prepared by heating the appropriate phenol (1*M*) with the halogenated fatty acid (1*M*) and caustic soda solution (2*M*) at 100° for 3 to 6 hours (*loc. cit.*). Some of the fluoro-aryloxy acids, which were obtained as oils, solidified on cooling. Others solidified when distilled under reduced pressure. These were characterised by determination of their neutralisation equivalents. The compounds obtained are shown in Table I.

TABLE I

Fluoro-aryloxy acid.	M.P. (obs.)	B.P. (obs.)	M.P. or B.P. (lit.)	% Yield.	Neut. equiv. Found.	Calc.
o - Fluoro-phenoxyacetic	138-39°	..	139°	77.0	169.9	170.0
o - Fluoro-phenoxypropionic	82-83°	..	..	84.2	182.5	184.0
o - Fluoro-phenoxybutyric	..	120-23°/ 70-80 mm	..	60.0	196.3	198.0
p - Fluoro-phnenoxyacetic	105°	..	105°	54.9	169.8	170.0
p - Fluoro-phenoxypropionic	93-94°	170-75°/ 55-60 mm	..	71.0	182.8	184.0
p - Fluoro-phenoxybutyric	..	170-75°/ 55-60 mm	..	56.6	198.5	198.0

Mercuration of Fluoro-aryloxy Fatty Acids.—The fluoro-aryloxy acids were mercurated by the method of Friend (*loc. cit.*) and Sen and Joshi (*loc. cit.*) Either a mixture of equimolecular quantities of mercuric acetate in water and fluoro-aryloxy acid in dilute acetic acid or a mixture with yellow mercuric oxide (1*M*) in 50% acetic acid solution was heated on a water-bath till a sandy powder separated. In some cases the mixture was refluxed for 2 hours over a low flame. The time required for the reaction varied from 1 to 6 hours. The precipitate was filtered and repeatedly washed with boiling water, hot dilute acetic acid and hot alcohol.

All the compounds are insoluble in water, dilute acids and common organic solvents, and are stable to air and light. When boiled with HCl (conc.), these are decomposed to mercuric chloride and the corresponding fluoro-aryloxy acid.

This solution was diluted with water, and mercury estimated as mercuric sulphide by passing H_2S into it, followed by washing the precipitate repeatedly with CS_2, ethanol and ether to dissolve sulphur and organic impurities (Vogel, *loc. cit.*, p. 504). The results of the analysis indicated that mono-mercurated anhydride of fluoro-aryloxy fatty acids were formed. The following mercury derivatives have been prepared.

TABLE II

	M.P.	% Mercury. Found.	Calc.
(1) $F.C_6H_3.(-O.CH_2.CO_2)-Hg$ (*o*)	230°	54.68	54.44
(2) $F.C_6H_3.(-O.CH_2.CO_2)-Hg$ (*p*)	> 250°	53.75	54.44
(3) $F.C_6H_3.(-O.CH.CH_3CO_2)-Hg$ (*o*)	* 120-23°	51.60	52.48
(4) $F.C_6H_3.(-O.CH.CH_3CO_2)-Hg$ (*p*)	* 125°	51.14	52.48
(5) $F.C_6H_3.(-O.CH.C_2H_5CO_2)-Hg$ (*o*)	* 123°	51.23	50.63
(6) $F.C_6H_3.(-O.CH.C_2H_5CO_2)-Hg$ (*p*)	* 164°	49.45	50.63

* The compounds partly melt and then decompose.

One of the authors (S.C.B.) is grateful to the Council of Scientific and Industrial Research, New Delhi, for the award of a junior research fellowship. The authors are thankful to Dr. R. C. Mehrotra, Professor and Head of the Chemistry Department, University of Gorakhpur, for providing all possible departmental facilities.

CHEMICAL LABORATORIES,
UNIVERSITY OF GORAKHPUR,
GORAKHPUR.

Received December 19, 1959.

[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

POSSIBLE ANTITUBERCULOUS COMPOUNDS. PART VIII. PREPARATION OF DIPHENYLAMINE-4-ARYL- OR -ALKYL-AMIDINES

By Vinay S. Misra and Md. Imtiaz Husain

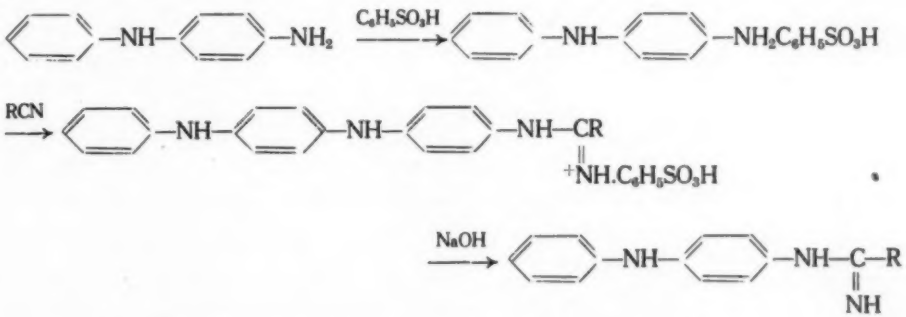
With a view to increasing the basic strength and surface area of *N*-4-diphenylamidines, compounds of known antitubercular activity, several diphenylamine-4-aryl- or -alkyl-amidines have been prepared.

In the present communication we have tried to increase the basicity and surface area of *N*-4-diphenylamidines by introducing a secondary nitrogen atom between the two benzene rings of diphenyl moiety and then preparing several new amidines from 4-aminodiphenylamine by adopting the usual method of Oxley and Short (*J. Chem. Soc.*, 1946, 147).

The 4-aminodiphenylamine was converted into 4-diphenylamine-ammonium benzenesulphonate by adopting the method of Bauer and Cymerman (*ibid.*, 1950, 1826). That the monosulphonate of 4-aminodiphenylamine was formed and not the disulphonate, was confirmed by the sulphur as well as nitrogen estimations. It was also envisaged that the addition of benzenesulphonic acid took place on the primary amino group and not on the secondary amino group of 4-aminodiphenylamine. This was confirmed by the failure of the dye test when applied to the 4-diphenylamine-ammonium benzenesulphonate.

The benzenesulphonate on fusing with an excess of benzo-, *o*-, *m*- and *p*-tolyl-, α- and β-naphtho-, butyro-, valero-, capro^{n}- and capro^{i}-nitriles at 230-40° yielded appropriate amidine-benzenesulphonates after repeated trituration with acetone or ether.

The amidine-benzenesulphonates were then converted into amidines by the usual method of basification and isolation. The latter were recrystallised either from chloroform-petroleum ether or from ethanol.



[R=Ph, tolyl (*o*-, *m*- & *p*-), naphthyl (α & β), C_3H_7, C_4H_9, $C_5H_{11}^{i}$ and $C_5H_{11}^{n}$]

The antitubercular activity of the amidines will be reported later on.

Experimental

(I). *4-Diphenylamine-ammonium Benzenesulphonate* (A).—4-Aminodiphenylamine (5.2g.) was suspended in dry ether (20 c.c.) and benzenesulphonic acid (6.0 g.), dissolved in methanol, was added to it dropwise under stirring. A light green solid separated out. It was filtered, dried and

recrystallised from hot water as a green amorphous powder, m.p. 204-205°, yield 9.0 g. (93%). (Found : N, 7.72 ; S, 8.88. $C_{18}H_{18}O_3N_2S$ requires N, 8.18 ; S, 9.35%).

TABLE I

Compounds. (R =)	M.P.	% Yield.	Recrystallised from.	Appearance (Powder).
Ph	163°	92	Ether	Brown
o-$C_6H_4CH_3$	245°	90	Acetone	,,
m-$C_6H_4CH_3$	145°	90	Ethanol	Dark brown
p-$C_6H_4CH_3$	190	50	Acetone	Brown
α-$C_{10}H_7$	115° (decomp.)	30	Ethanol	Black
β-$C_{10}H_7$	176-77°	76	Ether	Dark brown
C_3H_7	183°	85	Acetone	Grey
C_4H_9	146-47°	86	Ether	Brown
$C_5H_{11}^n$	167°	77	Do	Dark grey
$C_5H_{11}^i$	210°	16	Acetone	Dark brown

(II). *Diphenylamine-4-alkyl- or aryl-amidines.*—The compound (A) was converted into different amidine-benzenesulphonates and subsequently to corresponding free amidines, by adopting the usual method of their formation (Misra *et al.*, this *Journal*, 1952, **29,** 695 ; 1959, **36,** 270).

TABLE II

Amidine (R =).	M.P.	% Yield.	Appearance (Powder).	Formula	% Nitrogen. Found.	Calc.
Ph	85°	87	Green	$C_{19}H_{17}N_3$	14.14	14.63
o-$C_6H_4CH_3$	110°	75	Dark grey	$C_{20}H_{19}N_3$	14.35	13.95
m-$C_6H_4CH_3$	132-33°	83	Brown	$C_{20}H_{19}N_3$	14.20	13.95
p-$C_6H_4CH_3$	102°	68	Light grey	$C_{20}H_{19}N_3$	14.30	13.95
α-$C_{10}H_7$	170°	61	Black	$C_{23}H_{19}N_3$	12.10	12.46
β-$C_{10}H_7$	137-38°	66	Grey	$C_{23}H_{19}N_3$	12.77	12.46
C_3H_7	140°	5	Black	$C_{16}H_{19}N_3$	16.24	16.60
C_4H_9	161-162°	7	Black	$C_{17}H_{21}N_3$	16.00	15.70
$C_5H_{11}^n$	90°	6	Black	$C_{18}H_{23}N_3$	14.60	14.90
$C_5H_{11}^i$	157-58°	46	Brown	$C_{18}H_{23}N_3$	14.45	14.90

The authors are thankful to Dr. A. B. Sen, Professor and Head of the Department of Chemistry, Lucknow University, for his interest in the present work.

CHEMISTRY DEPARTMENT,
LUCKNOW UNIVERSITY,
LUCKNOW.

Received October 26, 1959.

[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

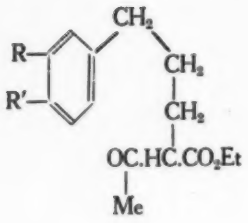
POLYCYCLIC SYSTEMS. PART VIII. SYNTHESIS OF SEVEN-MEMBERED RING COMPOUNDS

BY D. NASIPURI, R. ROY AND U. RAKSHIT

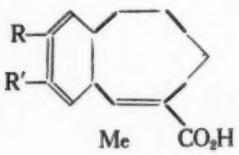
Several α-3-phenylpropyl-β-oxo-esters have been cyclised by polyphosphoric acid. Some of the substituted benzo*cyclo*heptene derivatives, thus obtained, have been employed for the synthesis of tricyclic systems (e.g.,X) having the skeletal structure of colchicine, the second seven-membered ring being built up by the Dieckmann ring-closure.

The cyclisation of appropriate aryl-substituted β-oxo-esters by means of concentrated sulphuric acid, first initiated by Bougault (*Compt. rend.*, 1914, **159,** 745) has received numerous applications in the synthesis of hydroaromatic compounds (cf. Pechmann, *Ber.*, 1883, **16,** 516; Auwers and Moller, *J. prakt. Chem.*, 1925, **109,** 124; Fieser and Hersberg, *J. Amer. Chem. Soc.*, 1935, **57,** 1851; Bachmann and Holmen, *ibid.*, 1951, **73,** 3660; Bardhan, *J. Chem. Soc.*, 1936, 1848; Bardhan and Nasipuri, *ibid.*, 1956, 350; Nasipuri, *ibid.*, 1958, 2618; Anner and Miescher, *Helv. Chim. Acta*, 1946, **29,** 586; Buchta and Güllich, *Chem. Ber.*, 1959, **92,** 1366). Extensive sulphonation and ester exchange (hydrolysis) are, however, some of the chief disadvantages of this method, specially in the case of higher aromatic systems. The use of sulphuric acid and phosphoric acid mixture (Crowley and Robinson, *J. Chem. Soc.*, 1938, 2001; Horning *et al.*, *J. Amer. Chem. Soc.*, 1951, **73,** 5830, 5826, 5828; Koo, *ibid.*, 1953, **75,** 1889) and, more recently, the use of polyphosphoric acid (Koo, *ibid.*, 1953, **75,** 1891) have eliminated these side reactions to a great extent and considerably increased the yield of the cyclisation. The last named reagent, besides avoiding the undesirable side-reactions, permits stronger reaction conditions and thus ensures better yields. During our synthetic investigations in seven-membered ring compounds (Guha and Nasipuri, *Science & Culture*, 1960, **25,** 492,) we felt that the Bougault-type of cyclisation of appropriately substituted β-oxo-esters (e.g., I) could be conveniently employed for the synthesisof polycyclic systems containing one or two seven-membered rings. A few cases of seven-membered ring-closure of this type are already in record (Koo, *J. Amer. Chem. Soc.*, 1953, **75,** 720, 723; Koo and Hartwell, *ibid.*, 1953, **75,** 1625). In view of the current interest in the synthesis of seven-membered ring compounds related to colchicine and analogues (Frank *et al.*, *ibid.*, 1948, **70,** 2314; Gutsche, *ibid.*, 1951, **73,** 786; Gutsche and Seligman, *ibid.*, 1953, **75,** 2579; Gutsche and Fleming, *ibid.*, 1954, **76,** 1771; Crabb and Schofield, *J. Chem. Soc.*, 1958, 4276, and references cited therein; Loewenthal and Rona, *Proc. Chem. Soc.*, 1958, 114; Schreiber *et al.*, *Angw. Chem.*, 1959, 637), we desire to report the results of our investigations.

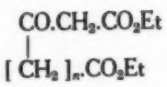
As guide experiments of seven-membered ring-closure, we investigated the cyclisation of a number of substituted ethyl α-3-phenylpropyl-β-oxobutyric esters (I : R = R′ = H or OMe) with polyphosphoric acid at the room temperature over a period of 1 to 5 hours. It was found that though ethyl α-3-phenylpropyl-β-oxobutyrate (I : R=R′=H) itself could not be cyclised to any appreciable extent by polyphosphoric acid, the methoxylated derivatives (I : R = OMe; R′=H and I : R=R′=OMe) underwent cyclisation smoothly and the resultant benzo*cyclo*heptene derivatives (II : R = OMe; R′=H), m.p. 137° and (II : R=R′=OMe), m.p. 178°, were isolated in about 70% yield. This result is in agreement with the observation of Koo (*loc. cit.*) that the cyclisation is facilitated to a certain extent by the presence of alkoxyl groups. The phenylpropyl alcohols, required for these experiments, were prepared in excellent yields by reduction of the corresponding cinnamic esters according to the procedure of Bouveault and Blanc.



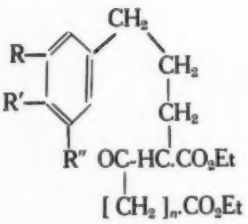
(I)



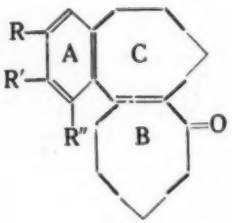
(II)



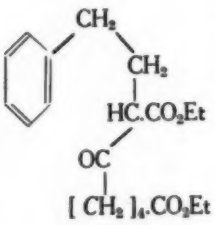
(III)



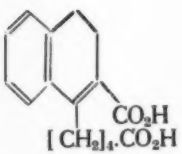
(IV)



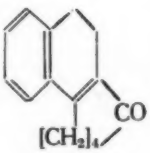
(V)



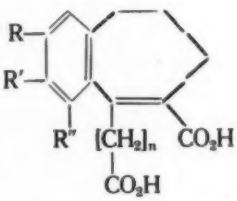
(VI)



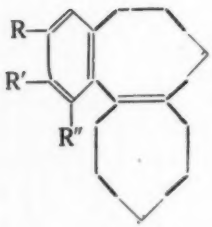
(VII)



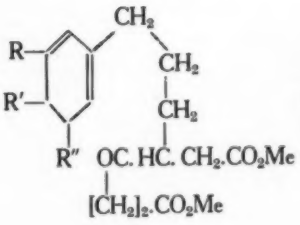
(VIII)



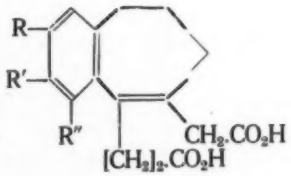
(IX)



(X)



(XI)



(XII)

The conditions of the ring-closure being thus established, the cyclisation of more complicated systems was next tried. Ethyl α-3-*m*-methoxyphenylpropyl-β-oxopimelate (IV : R = OMe ; R′ = R″ = H ; *n* = 3), obtained by alkylating ethyl β-oxopimelate (III : *n* = 3) (Guha, Rakshit and Nasipuri, this *Journal*, 1960, **37,** 267 ; Hunter and Hogg, *J. Amer. Chem. Soc.*, 1949, **71,** 1922) with 3-*m*-methoxyphenylpropyl bromide, on similar treatment with polyphosphoric acid and subsequent hydrolysis yielded the unsaturated acid (IX : R = OMe ; R′ = R″ = H ; *n* = 3), m.p. 175-76°. The dimethyl ester of the latter on the Dieckmann cyclisation, followed by hydrolysis, furnished the tricyclic ketone (V : R = OMe ; R′ = R″ = H, with ring-B six-membered). In another experiment, phenethyl bromide was condensed with ethyl β-oxosuberate (III : *n* = 4) (Archer and Pratt, *ibid.*, 1944, **66,** 1656) and the resultant β-oxo-ester (VI) cyclodehydrated with concentrated sulphuric

acid (Bardhan and Nasipuri, *J. Chem. Soc.*, 1956, 350) to yield δ-(2-carboxy-3 :4-dihydro-1-naphthyl)-valeric acid (VII), m.p. 124-25° in an excellent yield. Heating the corresponding dimethyl ester with powdered sodium in xylene and subsequent hydrolysis afforded the ketone (VIII).

Finally, it was intended, by suitable application of the Bougault cyclisation and the Dieckmann ring-closure, to synthesise compounds with two seven-membered rings. For this purpose, and with a view to synthesising octahydrodemethoxydeoxydeacetamidocolchicine (X : R = R′ = R″ = OMe) (Rapoport *et al.*, *J. Amer. Chem. Soc.*, 1954, **76,** 3693), ethyl ester of 3 :4 :5-trimethoxycinnamic acid (Rapoport and Campion, *ibid.*, 1951, **73,** 2239) was reduced by sodium and ethanol. But instead of the desired γ-3 :4 :5-trimethoxyphenylpropanol, γ-3 : 5-dimethoxyphenylpropanol was obtained in 60% yield, the 4-methoxyl group being completely eliminated during reduction. Replacement of the central methoxyl group in a trimethylpyrogallol system by hydrogen during similar reduction is, however, quite well known (cf. Asahina, *Ber.*, 1936, **69B,** 1643 ; Christiansen *et al.*, *J Amer. Chem. Soc.*, 1955, **77,** 948). Though failed in our original purpose, this reaction, nevertheless, might serve as a good preparative method for γ-3 : 5-dimethoxyphenylpropanol, which is difficult to obtain otherwise.

The bromide of the above alcohol was condensed with ethyl β-oxosuberate in the usual manner and the resultant β-oxo-ester (IV : R′ = H ; R = R″ = OMe ; n=4) cyclodehydrated with polyphosphoric acid. The gummy dicarboxylic acid (IX : R=R″=OMe ; R′=H ; n=4), obtained by hydrolysing the cyclised product, was purified through the dimethyl ester and the latter cyclised by heating with powdered potassium in toluene for 10 hrs. The product on hydrolysis afforded a ketone (V : R = R″ = OMe ; R′ = H), m.p. 135° in about 20% yield. The latter on the Huang-Minlon reduction (Huang-Minlon, *ibid.*, 1946, **68,** 2487) furnished the deoxy compound (X : R=R″=OMe ; R′ = H), m.p. 55-56°. The epoxy derivative, prepared by perbenzoic acid oxidation, melted at 121-23°. The ultraviolet absorption spectra of the deoxy compound are very similar to those of octahydrodemethoxydeoxydeacetamidocolchicine (X : R=R′=R″=OMe) (Rapoport *et al.*, *loc. cit.*). A synthesis of the latter from γ-3 : 4 : 5-trimethoxyphenylpropanol (Nasipuri, Rakshit and Guha, *Proc. Indian Sci. Cong.*, 1960, Part III, p. 147) through the above sequence of reaction will shortly be reported elsewhere.

Investigations are being carried out at present, for the synthesis of the dicarboxylic acid (XII) through the cyclisation of the keto-ester (XI). The latter has been prepared by alkylation of the β-oxo-ester (IV : R =R′=R″=OMe ; n=2) with ethyl bromoacetate, followed by hydrolysis and esterification (cf. Nasipuri, *Chem. & Ind.*, 1956, 1389). The dicarboxylic acid (XII) will subsequently be used as a starting material for the synthesis of colchicine and analogues.

EXPERIMENTAL

γ-3-Methoxy- and 3 : 4-*dimethoxyphenylpropanols* required in these experiments were prepared from the corresponding cinnamic acids. The latter were obtained in good yields from methoxylated benzaldehydes according to the procedure of Livshits *et al.* (*J. Gen. Chem. U.S.S.R.*, 1947, **17,** 1671). In a typical preparation, 3 :4-dimethoxybenzaldehyde (25 g.), malonic acid (32 g.), pyridine (50 c.c.) and piperidine (1 c.c.) were heated at 80° for 1 hr. and then for 2 hrs. at 100° and for 0.5 hr. at gentle reflux. The mixture was poured into excess of 12% HCl, filtered, washed, and dried to afford 3 :4-dimethoxycinnamic acid (26 g.), m.p. 178-80°. Horning *et al.* (*loc. cit.*) record m.p. 180°. *m*-Methoxycinnamic acid, prepared in the same way, melted at 115°. The ethyl esters were obtained in the usual way by refluxing ethanol with sulphuric acid as catalyst The esters were reduced by sodium and ethanol according to the following procedure.

A solution of ethyl 3 :4-dimethoxycinnamate (26 g., m.p. 55-56°) in super-dry ethanol (160 c.c.) was added all at once to finely divided sodium (30 g.), preheated to a temperature of 80°. The temperature of the oil-bath was then raised to 135° and the molten sodium was pulverised by shaking the flask vigorously. When all the sodium had gone into solution (2 hrs.), the heating at 135° was continued for 2 hrs. more with the occasional addition of ethanol (3×20 c.c.). The cooled mixture was next decomposed with water (200 c.c.) and most of the alcohol removed by steam distillation. γ-3 : 4-*Dimethoxyphenylpropanol* was worked up in the usual way and distilled to furnish a colorless oil (13 g., 58%), b.p. 160-65°/2 mm. The alcohol formed 3 :5-*dinitrobenzoate* readily which crystallised from ethanol in yellow needles, m.p. 110°. (Found : C, 55.2 ; H, 4.8 ; N, 7.3. $C_{18}H_{18}O_8N_2$ requires C, 55.4 ; H, 4.6 ; N, 7.2%).

The corresponding phenylpropyl bromide was prepared by treating the preceding alcohol (10 g.) with PBr_3 (7.5 g.) in CCl_4 (15 c.c.) at 60° for 30 mins. γ-3 :4-*Dimethoxyphenylpropyl bromide* distilled at 145°/2mm. (Found : Br, 30.4. $C_{11}H_{15}O_2Br$ requires Br, 30.8%).

Ethyl α-3-*Phenylpropyl*-β-*oxobutyrate* (I : R=R′=H).—To a cold mixture of ethyl acetoacetate (13 g.) and ethanolic sodium ethoxide (from sodium 2.3 g. and ethanol 50 c.c.) was added γ-phenylpropyl bromide (20 g.) and the whole was heated under reflux at 90° for 8 hrs. After removal of most of the ethanol, the residue was treated with cold 2*N*-H_2SO_4 and the organic matter taken up in ether. The ethereal extract was washed with water, dried and evaporated. The residue was distilled to furnish the β-*oxo-ester* (I : R=R′=H), b.p. 160-65°/2 mm. (Found : C,72.5 ; H, 8.3. $C_{15}H_{20}O_3$ requires C, 72.6 ; H, 8.0%).

Ethyl α-3-m-*Methoxyphenylpropyl*-β-*oxobutyrate* (I : R=CMe ; R′=H), b.p. 175-77°/0.8 mm (Found : C, 68.8 ; H, 8.2. $C_{16}H_{22}O_4$ requires C, 69.1 ; H, 7.9%) and *ethyl* α-3-(3 : 4-*dimethoxyphenyl*) *propyl*-β-*oxobutyrate* (I : R=R′=OMe), b.p. 190-95°/0.3 mm (Found : C, 66.0 ; H, 7.9. $C_{17}H_{24}O_5$ requires C, 66.2 ; H, 7.7%) were prepared in the identical way.

5′-*Methoxy- and* 4′ :5′-*Dimethoxy*-1 :2-*benzo*cyclo*hept*-1 : 3-*diene*-3-*methyl*-4-*carboxylic Acids* (II : R=OMe ; R′=H and II : R=R′=OMe).—(*a*). *Ethyl* α-3-*m*-methoxyphenylpropyl-β-oxobutyrate (I : R=OMe ; R′=H) (2 g.) was kept in with polyphosphoric acid, prepared from phosphorus pentoxide (12 g.) and 89% phosphoric acid (10 c.c.) at room temperature for 1 hr. The red mixture was decomposed with ice-water and extracted thoroughly with ether. The ethereal layer was washed with sodium bicarbonate solution, and then with water, dried, and the solvent evaporated to afford a neutral product (1.1 g.). This was hydrolysed with ethanolic KOH and the *acid* (II : R=OMe ; R′=H) (1 g.), thus obtained, was crystallised from methanol to furnish needles, m.p. 137°. (Found : C, 72.3 ; H, 7.1 ; equiv., 232. $C_{14}H_{16}O_3$ requires C, 72.4 ; H, 6.9% ; equiv., 232). The sodium bicarbonate extract on acidification yielded a further crop of the crystalline acid (0.3 g.), m.p. 130-32°.

Ethyl α-3-(3 : 4-dimethoxyphenyl)propyl-β-oxobutyrate (I : R=R′=OMe) on similar treatment afforded 4 : 5′-*dimethoxy*-1 : 2-*benzo*cyclo*hept*-1 : 3-*diene*-3-*methyl*-4-*carboxylic acid* (II : R=R′=OMe), m.p. 178°, yield 70%. (Found : C, 68.5 ; H, 6.9 ; equiv., 261. $C_{15}H_{18}O_4$ requires C, 68.7 ; H, 6.8% ; equiv., 262). The yield could not be appreciably increased on prolonging the period of treatment with polyphosphoric acid to 5 hrs. or even more.

(*b*). Attempts to cyclise the β-oxo-ester (I : R=R′=OMe) with concentrated sulphuric acid (5 vol.) at 0° for 2-3 hrs. did not succeed.

Ethyl α-3-m-*Methoxyphenylpropyl*-β-*oxopimelate* (IV: R=OMe ; R′=R″=H; *n*=3).—*m*-Methoxyphenylpropyl bromide (23 g.) was condensed with ethyl 4 :6-dioxoheptane-1 :5-dicarboxylate (27.2 g.) (Bardhan and Nasipuri, *loc. cit.*) in presence of ethanolic sodium ethoxide (from

sodium 2.3 g. and ethanol 40 c.c.) by heating the mixture at 90° for 10 hrs. It was then diluted with water, acidified and repeatedly extracted with ether. The ethereal solution was washed with water, dried (Na_2SO_4) and evaporated. The *β-oxo-ester* was finally obtained as a colorless oil (22 g.), b.p. 210-20°/0.6 mm. (Found : C, 66.8 ; H, 7.4. $C_{21}H_{30}O_6$ requires C, 66.6 ; H, 7.9%).

5′-Methoxy-1 : 2-benzocyclohept-1 : 3-diene-4-carboxyl-3-γ-butyric Acid (IX : R=OMe ; R′ = R″=H ; *n*=3).— The preceding β-oxo-ester (9 g.) was treated with polyphosphoric acid (120 g.) for 5 hrs. at room temperature. The product was worked up as before and hydrolysed by boiling with 5% methanolic KOH solution to yield the crude *dicarboxylic acid* (5 g.) as a semisolid mass. The acid on several crystallisations from aqueous methanol was finally obtained in colorless needles (1 g.), m.p. 174-76°. (Found : C, 66.8 ; H, 6.6 ; equiv., 154. $C_{17}H_{20}O_5$ requires C, 67.1 ; H, 6.5% ; equiv., 152).

The *dimethyl ester* was prepared in the usual way by refluxing the acid with methanolic sulphuric acid, and had b.p. 210-12°/0.5mm.

1′ : 2′ : 3′ : 4′-Tetrahydro-7′-methoxy-1′-oxo-1 : 2 : 3 : 4-dibenzocyclohept-1 : 3-diene (V : R = OMe ; R′=R″=H ; ring-B six-membered).— The foregoing ester (1.6 g.) was added to a suspension of 'molecularised' sodium (0.12 g.) in dry thiophen-free benzene (5 c.c.) containing 2 drops of methanol, and the mixture refluxed for 4 hrs. The resulting *β-oxo-ester* was worked up in the usual way and hydrolysed with refluxing glacial acetic acid (20 c.c.), HCl (conc., 10 c.c.) and water (2 c.c.) for 30 mins. The *ketone* (0.5 g.) was purified through chromatography over alumina and afforded a red *dinitrophenylhydrazone* (from chloroform and methanol), m.p. 250-52°. (Found : C, 62.30 ; H, 5.2 ; N, 13.2. $C_{22}H_{22}O_5N_4$ requires C, 62.6 ; H, 5.2 ; N, 13.3%).

Ethyl α-Phenethyl-β-oxosuberate (VI).— Phenethyl bromide (22 g.) was condensed with ethyl β-oxosuberate (30 g.) (III : *n*=4) in presence of sodium ethoxide, prepared from sodium (3 g.) and absolute ethanol (50 c.c.), in the same way as described before. The condensation product, worked up in the usual way, on distillation furnished the *β-oxo-ester* (VI) as colorless oil (16.5 g.), b.p. 200-10°/0.4 mm. (Found : C, 68.7 ; H, 8.1. $C_{20}H_{28}O_5$ requires C, 68. 9 ; H, 8.0%).

2-Carboxy-3 :4-dihydro-1-naphthyl-δ-valeric Acid (VII).—The above β-oxo-ester (10 g.) was slowly added to well-stirred H_2SO_4 (conc., 65 c.c.), cooled in a freezing mixture. After allowing the mixture to stand for 3 hrs. at −5° to −10°, it was poured on crushed ice when a semisolid mass separated, which was extracted with ether. The residue after evaporation of the ether was hydrolysed with boiling ethanolic KOH (KOH 7 g., water 7 c.c. and ethanol 100 c.c.) for 3 hrs., affording the crude *dicarboxylic acid* (VII) (5.6 g.). On repeated crystallisation from benzene-petroleum ether (40-60°) it was obtained in thick prisms, m.p. 124-25°. (Found : C, 69.8 ; H, 6.4 ; equiv., 137. $C_{16}H_{18}O_4$ requires C, 70.1 ; H, 6.6% ; equiv., 137).

The acid (5.5 g.) was heated with a mixture of methanol (50 c.c.) and H_2SO_4 (conc., 3 c.c.) for 6 hrs., and the product on distillation furnished the *dimethyl ester* (5 g.), b.p. 180-90°/0.8 mm. (Found : C, 71.2 ; H, 7.4. $C_{18}H_{22}0_4$ requires C, 71.5 ; H, 7.3%).

1′ : 2′-Dihydro-3′ :4′-naphtho-2 :3-cyclohept-2-en-1-one (VIII).—The foregoing ester (3 g.) was refluxed with a mixture of pulverised sodium (1 g.), dry xylene (30 c.c.)and methanol (2 drops.) for 4 hrs. in nitrogen atmosphere. The resulting sodio-salt was then decomposed with water (100 c.c.), acidified with HCl and extracted with benzene. The residue after evaporation of the benzene was hydrolysed with boiling 0.5 *N* ethanolic KOH solution (100 c.c.) for 3 hrs. After removal of most of the ethanol, the organic matter was taken up in ether, the ethereal layer thoroughly washed with sodium carbonate solution, then with water, dried, and the solvent evaporated. The residue was distilled in high *vacuo* to furnish the *ketone* (VIII) as an oil (0.8 g.), b.p. 145-50°/0.2 mm. It

formed a *dinitrophenylhydrazone* which crystallised from ethyl acetate in dark red needles, m.p. 194°. (Found : C, 64.0 ; H, 4.9 ; N, 14.2. $C_{21}H_{20}O_4N_4$ requires, C, 64.3 ; H, 5.1 ; N, 14.3%).

γ-3 :5-*Dimethoxyphenylpropanol*.—3 :4 :5-Trimethoxybenzaldehyde, prepared according to Cook *et al.* (*J. Chem. Soc.*, 1944, 322), was converted into 3 : 4 : 5-trimethoxycinnamic acid in the same way as described before. The ethyl ester (20 g.) of the cinnamic acid was dissolved in super-dry ethanol (130 c.c.) and was added to sodium (25 g.), preheated to 80° in a flask fitted with an efficient condenser. The mixture was then heated rapidly to 135° in an oil-bath and the molten sodium was finely dispersed by shaking the flask vigorously several times. Heating was continued at 135-40° for 5 hrs. more with a further addition of ethanol (2×30 c.c.) towards the end, to ensure complete dissolution of sodium. The cooled mixture was then decomposed with water (100 c.c.) and the ethanol removed by steam distillation. The product on being worked up in the usual way afforded γ-3 :5-*dimethoxyphenylpropanol* (9 g., 60%), b.p. 165°/0.2 mm. (Found : C, 67.4 ; H, 8.4. $C_{11}H_{16}O_3$ requires C, 67.3 ; H, 8.2%). It formed 3 : 5-*dinitrobenzoate*, m.p. 141° (ethanol). (Found : C, 55.2 ; H, 4.8 ; N, 7.4 ; OMe, 15.7. $C_{18}H_{18}O_8N_2$ requires C, 55.4 ; H, 4.6 ; N, 7.2 ; OMe, 15.8%).

γ-3 :5-*Dimethoxyphenylpropyl Bromide*.—A solution of the above alcohol (8 g.) in dry CCl_4 (10 c.c.) was treated with PBr_3 (1.8 c.c.) at 60° for 30 mins. The mixture was then poured over ice and the product worked up in the usual way to yield the *bromide* (8 g.), b.p. 140-45°/0.2 mm. (Found : C, 50.7 ; H, 6.0. $C_{11}H_{15}O_2Br$ requires C, 50.9 ; H, 5.8%).

3′ :5′-*Dimethoxy*-1 :2-*benzocyclohept*-1 :3-*diene*-4-*carboxyl*-3-δ-*valeric Acid* (IX : R=R″=OMe ; R′=H ; *n*=4).— Ethyl β-oxosuberate (10 g.) was added to a stirred solution of potassium (1.4 g.) in dry butanol[1] (28 c.c.) in nitrogen atmosphere. γ-3 :5-Dimethoxyphenylpropyl bromide (9.0 g.) was then rapidly added and the mixture heated under reflux for 12 hrs. Most of the alcohol was removed in the water-pump, the rest decomposed with acidulated water and extracted with ether. The ethereal solution was washed with water, dried, and the solvent evaporated. Fractions boiling up to 150°/0.2 mm were removed by distillation and the residue, which mainly consisted of the β-*oxo-ester* (IV : R=R″=OMe ; R′=H ; *n*=4), was used directly for cyclodehydration.

The above β-oxo-ester (3 g.) was kept in with polyphosphoric acid, prepared from 85% phosphoric acid (15 c.c.) and phosphorus pentoxide (20 g.), at room temperature for 5 hrs. The deep red solution was decomposed with ice and worked up as usual. The product on hydrolysis afforded the *dicarboxylic acid* (IX : R=R″=OMe ; R′=H ; *n*=4) (1.9 g.) as gum which could not be induced to crystallise. It was directly esterified with methanolic sulphuric acid, and the *dimethyl ester* obtained as viscous oil, b.p. 220-25°/0.2 mm. A good middle fraction was analysed. (Found : C, 67.6 ; H, 7.9. $C_{21}H_{28}O_6$ requires C, 67.0 ; H,7.4%).

5 :6 :7 :8 :9 :10 :11 :12-*Octahydro*-1 :3-*dimethoxy*-8-*oxobenzo* [*a*] *heptalene* (V : R=R″=OMe; R′=H).—The preceding ester (3 g.) in dry toluene (40 c.c.) was added during 1 hr. to a boiling suspension of potassium (1 g.) in toluene (15 c.c.) with vigorous stirring in nitrogen atmosphere. The reflux was continued for 8 hrs. more, the mixture cooled and decomposed with water. The organic matter was extracted with benzene, washed with water and the solvent evaporated in the water-pump. The residue (3 g.) was kept overnight with a solution of methanol (70 c.c.), potassium hydroxide (4 g.), and water (8 c.c.). Next day it was refluxed for one hour, acidified with HCl (22 c.c.) and heated for further 8 hrs. Methanol was then removed from the water-bath, organic layer extracted with benzene, washed with water, dried, and the solvent evaporated. The residual viscous oil (1 g.) was taken up in benzene and absorbed in an alumina column, and eluted with a mixture of benzene and petroleum ether (40-60°). The *ketone* (V ; R=R″=OMe ; R′=H) was

finally obtained in fine needles from methanol (400 mg.), m.p. 135°. (Found : C, 75.4 ; H, 7.8. $C_{18}H_{22}O_3$ requires C, 75.5; H, 7.6%). The *dinitrophenylhydrazone* was crystallised from ethyl acetate-methanol in silky red needles, m.p. 239-40°. (Found : C, 61.4 ; H, 5.8 ; N, 12.1. $C_{24}H_{26}O_6N_4$ requires C, 61.8 ; H,5.6 ; N, 12.0%).

5 : 6 : 7 : 8 : 9 : 10 : 11 : 12-*Octahydro*-1 : 3-*dimethoxybenzo* [*a*]*heptalene* (X : R=R″=OMe ; R′=H).—A mixture of the foregoing ketone (200 mg.), KOH (180 mg.), diethyleneglycol (3 c.c.), and 80% hydrazine hydrate (0.2 c.c.) was heated under reflux for 1½ hrs. Water was then distilled off until the temperature rose to 195°, when refluxing was continued for 4 hrs. longer. The cooled solution was diluted with water, acidified with HCl, and extracted with benzene (3×20 c.c.). The residue after evaporation of benzene was shaken for 2 hours at room temperature with 3*N*-NaOH (35 c.c.) and dimethyl sulphate (5 c.c.). The solution was then extracted with ether, washed with water, dried, and the solvent removed. The residue was passed through an alumina column in petroleum ether solution and the *deoxy compound* (X : R=R″=OMe ; R′=H) was finally purified by sublimation and crystallised from pertoleum ether (b.p. 60-80°) in colorless needles, m.p. 55-56° ; λ_{max}^{EtOH} 256 and 283 mμ (log ε 4.00 and 3.80 respectively). (Found : C, 79.3 ; H, 8.9 ; OMe, 23.0. $C_{18}H_{24}O_2$ requires C, 79.4 ; H, 8.8 ; OMe, 22.8%).

Epoxidation of (X : R=R″=OMe ; R′=H).—The above deoxy compound (40 mg.) and 0.04*M* perbenzoic acid solution (16 c.c.) in chloroform were left for 4 hrs. at 0°, and then decomposed by the addition of *N*-K_2CO_3 solution (10 c.c.). The chloroform layer was separated, washed with water, dried, and the solvent evaporated. The residual solid was chromatographed (alumina) and crystallised from petroleum ether (b.p. 40-60°) in needles, m.p. 121-23°. (Found : C, 74.8; H, 8.5. $C_{18}H_{24}O_3$ requires C, 75.0 ; H, 8.3%).

Methyl 4-*Carbomethoxymethyl*-3-*oxo*-7-(3 : 4 : 5-*trimethoxyphenyl*)*heptane*-1-*carboxylate* (XI : R=R′=R″=OMe).— γ-3 : 4 : 5-Trimethoxyphenylpropanol, prepared according to the method of Rapoport and Campion (*loc. cit.*), was converted into its *bromide*, b.p. 160-62°/2 mm, by the action of PBr_3 (*vide supra*). The bromide (29 g.) was condensed with ethyl β-oxoadipate (22 g.) in presence of potassium butylate[1] (from potassium 4 g. and butanol[1] 80 c.c.) by heating in the water-bath for 10 hrs. in nitrogen atmosphere. After removal of some of the alcohol in the water-pump, the residue was decomposed with acidulated water, extracted with ether, dried, and the solvent evaporated. The residue was distilled up to 150°/0.2 mm to remove low-boiling impurities as far as possible. The rest was treated with a solution of sodium (2.3 g.) in ethanol (50 c.c.), cooled, and ethyl bromoacetate (17 g.) was added. Next day, the mixture was refluxed on the water-bath for 6 hrs. and the product worked up in the usual way. The crude material (40 g.) was directly hydrolysed by refluxing with 2% aqueous NaOH solution (1 litre) for 10 hrs. The neutral matter was extracted with ether, the alkaline solution acidified, and the organic matter was taken up in ether. The ethereal solution was dried (Na_2SO_4), solvent evaporated, and the residue (23 g.) was esterified by heating with 3% methanolic HCl (300 c.c.). The product was worked up in the usual way, and on distillation afforded the *ester* (XI : R=R′=R″=OMe) as viscous oil (15 g.), b.p. 220-30°/0.2 mm. A middle fraction was analysed. (Found : C, 61.7 ; H, 7.5. $C_{21}H_{30}O_8$ requires C, 61.5 ; H, 7.3%).

The cyclisation of the ester by means of polyphosphoric acid is under investigation.

Department of Organic Chemistry,
University College of Science,
Calcutta-9.

Received February 18, 1960.

OBITUARY

DR. RAMESH CHANDRA RAY

Born : 20.1.1890. Died : 3.12.1959.

Ramesh Chandra Ray was born on the 20th January 1890 at Ranchi in Bihar. He had his early education at the Ranchi Zilla School. He went to the Presidency College, Calcutta for his University education, where he graduated (B.Sc.) with Honours in Physiology in 1909. Two years later he secured the degree of Master of Science in Chemistry, specialising in Inorganic Chemistry. He next migrated to Bangalore to work under the guidance of Prof. Morris W. Travers, F.R.S.. the first Director of the Indian Institute of Science. His work under Travers on *Borohydrates*, (1912-14) qualified him for the Associateship of the Institute.

He joined the Patna College, Patna, in 1915 as Assistant Professor of Chemistry in the Bihar and Orissa Educational Service. He went on study leave for 2 years, 1921-23, to London where he joined the laboratory of Prof. F.G. Donnan, F.R.S. His work in London on quartz, the salts of borohydrates and adsorption earned him the degree of Doctor of Science of the London University.

He returned to India towards the end of 1923 and rejoined his post at the Patna College. He was promoted to a Professorship in 1927 and posted to the newly established Patna Science College as Professor of Inorganic Chemistry. In 1940, he became the Head of the Department and in addition to these duties was appointed Chemical Adviser to the Government of Bihar. He retired from Government service in 1946 and in recognition of his long and distinguished service in the cause of science and education, the Government of India conferred on him the title of Rai Bahadur.

The volume of Ray's published work, about 25 papers, does not convey the full significance of the role he played in the development of scientific research, particularly in the field of Inorganic Chemistry, and in the creation of research atmosphere in this country. Facilities for research in the Patna College in the early years of his career were meagre and teaching work was heavy. Neither was the administrative atmosphere of a postitively encouraging type. It needed a lot of enthusiasm and grim determination for scientists in those circumstances to pursue research work in most of the teaching institutions in the coutnry. The elegant and precise work of Dr. Ray has to be viewed against this background. His interest, roused in Prof. Traver's laboratory, on the products of hydrolysis of magnesium boride, persisted right through his life and it was a treat to hear him speak of the various compounds he isolated as though he was narrating the biographical details of his friends. He initiated and guided work on phase rule studies, adsorption and complex compounds.

Academic and professional honours came to him without his seeking. He was elected a Fellow of the National Institute of Sciences, India in 1943. The Patna University elected him to deliver the Sukhraj Ray Readership lectures in 1944. The Indian Science Congress elected him as the President of its Chemistry section in 1944.

Dr. Ray was a distinguished teacher. He was held in high esteem, by all who knew him, for his integrity, character and devotion to duty. His death, which occurred on December 3, 1959, removes from the scene of Indian science an erudite chemist. His friends and students will miss a serene and genuine friend.

P. C. Sinha.

REVIEW

Robert Boyle & Seventeenth-Century Chemistry—by Marie Boas, Cambridge University Press, 1958. Pages 236. Price 30sh. net.

The volume presents an authentic account of the life and work of Robert Boyle and the development of chemistry during the seventeenth century, which, as the author has shown, was influenced enormously by Boyle's ideas and his scientific method of experimentation. Boyle Papers (manuscripts) and Boyle Letters, preserved in the library of the Royal Society, as well as several published works of Boyle, of which special mention may be made of the *Sceptical Chymist*, form the main source of author's information. There prevails a general impression that seventeenth-century chemistry was dominated by mystic alchemical ideas and iatrochemical interest with exclusive attention to the preparation of drugs. In fact, till the middle of that century, chemistry was seldom regarded as a part of natural philosophy, and the physicists used to pay scant courtesy to it. The author has, however, tried to correct this impression from a critical study of Boyle's work and those of his contemporaries.

Though with a public reputation as one of the prominent physicists of the time, Boyle thought of himself as primarily a chemist, and by his contributions towards the better understanding of chemical composition, the development of tests for identification of chemical substances, the rational explanation and elucidation of chemical reactions, and the improvement of chemical classification and nomenclature, paved the way for the recognition of chemistry as a branch of natural philosophy. The work of Boyle and of the contemporary chemists of the later seventeenth century served as the formulation of problems for Lavoisier and the chemists of the eighteenth century to solve, and thus to build upon the ground prepared by the former. All these have been brought to light in a convincing manner by the author of the book, quoting often from Boyle's writings.

Boyle was widely known throughout the continent not only as a great English physicist because of his work on pneumatics and air-pump, but also as a leading English chemist. The author has, therefore, rightly observed that "Boyle became the leader in developing and promoting a new kind of chemistry, a chemistry which was soon to change and improve the development of natural philosophy". As one of the founders and organizers of the Royal Society, Boyle with his great interest in the pursuit of chemistry contributed in no small measure to elevate its status for recognition as a real and independent branch of science and not at best a mere art in the service of medicine. In fact, Boyle used to define chemistry as "speculative physics (if one considers theory) and practical physics (if one considers practice)". A similar observation has been quoted by the author from Boyle's writings which appeared in 1661 under the title *Physiological Essays*, where Boyle made the statement "some Men care only to know Nature, others desire to command Her". The first obviously refers to theoretical philosophy and the second to experimental philosophy to which Boyle thought chemistry to be the key.

Boyle, along with Newton, used to believe in a particulate or corpuscular theory of matter, and he utilized his chemical experiments in support of this theory. The author, therefore, has made the pertinent observation, "alone among chemists Boyle was a natural philosopher who regarded

a physical theory of matter as one which was necessary to the clear understanding of chemistry..... and so he worked to banish all occult forces from chemistry as well as from natural philosophy, and all by means of his corpuscular philosophy".

Boyle was a superb experimenter, but in trying to use their results for the support and development of his theory he made himself often incomprehensible. His method of writing, as the author observes, was rather confusing, verging almost on obscurity, a common failing of the seventeenth-century English scientists. But so far as the experiments are concerned, the author has pointed out that Boyle may be said to be the forerunner of Lavoisier in applying the quantitative method to chemistry. Boyle prepared an excellent and methodical list of chemical tests for analytical work of testing acidity and alkalinity, and for the detection of iron, sulphur, copper vitriol, arsenic, etc. The author has also shown that Boyle was a pioneer in suggesting the use of balance for determining specific gravity for chemical identification, just as he was a pioneer in the application of physical thinking to chemical problems.

The author has thus succeeded in demonstrating that the chemistry of the seventeenth century was but a prelude to that of the eighteenth century in many respects, mainly through the work of Boyle who spared no efforts to propagate the idea that chemistry and natural philosophy are inseparable and closely linked together. The author, therefore, aptly concludes :

"In a quiet way eighteenth-century chemists built upon seventeenth-century theoretical achievements to the great advantage of the progress of chemistry. It was no mean accomplishment.

"The amalgamation of chemistry and physics, and the development of rational chemical theory in chemistry, amply indicate that the seventeenth-century chemistry deserves a place in the seventeenth-century scientific revolution.

"Boyle and his contemporaries did raise chemistry to a point where physicists recognized it as a real and important science, working in the same spirit as contemporary natural philosophy".

Dr. Boas has made a powerful critical analysis of Boyle's work and of the position and development of chemistry as a science in the seventeenth century. The book is written in an interesting and readable style, and a very useful bibliography has been added at the end. The printing and get-up leave nothing to be desired, though the price is somewhat high.

In the opinion of the reviewer the book constitutes a valuable contribution to the history of science, and should find a place in the libraries of all scientific institutions.

P. Rây

For Laboratory Reagent Quality Acids

To Precise Specifications

Maximum Limits of Impurities :	**Acid Sulphuric** H_2SO_4 : 98% w/w Sp. gr. 1.840 at 15°.	**Acid Nitric** HNO_3 : 69.8% w/w Sp. gr. 1.420 at 15°.	**Acid Hydrochloric** HCl:35.4% w/w Sp. gr. 1.180 at 15°.
Non-Volatile Matter :	0.0025%	0.01%	0.001%
Chloride (Cl) :	0.0002%	0.00007%	—
Free Chlorine (Cl) :	—	—	0.0002%
Nitrate (NO_3) :	0.00002%	—	—
Sulphate (SO_4) :	—	0.0003%	0.0003%
Heavy Metals (Pb) :	0.0002%	0.0002%	0.0002%
Iron (Fe) :	0.0001%	0.0001%	0.0001%
Arsenic (As) :	0.1 part per million	0.02 part per million	0.04 part per million
Ammonium (NH_4) :	0.0005%	—	—
Selenium (Se) :	0.001%	—	—
Oxygen Absorbed (O) :	0.00015%	—	—

We invite orders and enquiries.
Write us about your requirements
for other reagent quality chemicals.

Bengal Chemical & Pharmaceutical Works, Ltd.

CALCUTTA :: BOMBAY :: KANPUR

Office: 6, Ganesh Chunder Avenue, Calcutta-13

Gram : LILICOM CALCUTTA Phone : 23-1316

LILICO PRIVATE LIMITED.

3, MANGOE LANE, CALCUTTA-1

DISTRIBUTORS OF

WHATMAN FILTER PAPERS

FINE CHEMICALS

FOR ANALYTICAL, PHARMACEUTICAL, PHOTOGRAPHIC, RESEARCH AND TECHNICAL PURPOSES

STANDARD STAINS AND INDICATORS : PRODUCTS OF M/S. HOPKIN & WILLIAMS LTD. & L. LIGHT & CO., LTD.

AVOSET SUGAR OF MILK (U.S.A.)

IMPORTERS & DEALERS IN

FILTER PAPERS, CHEMICALS, LABORATORY REQUISITES, APPARATUS ETC.

Enquiries Solicited from

IMPORTERS, DEALERS & USERS

GS Gas PLANTS

FOR

HEATING

IN

LABORATORY

INDUSTRY

KITCHEN

GANSONS

PRIVATE LIMITED.

P.O.B. 5576, BOMBAY-14.

—Also makers of—

Superior Laboratory Fittings

Atomic Equipments.

Sigcol

LABORATORY GLASS APPARATUS

Sole Selling Agents :

GHARPURE & CO.

P-36, ROYAL EXCHANGE PLACE EXTN. CALCUTTA-1

Gram : MEENAMO. Phone : 22-2061

BOROSIL

LABORATORY GLASSWARE

such as

FLASKS, BEAKERS, CONDENSERS, MEASURING FLASKS, MEASURING CYLINDERS, PIPETTES & ANY SPECIAL APPARATUS MADE TO DESIGN

and

PENICILLIN VIALS, VACCINE BULBS—WHITE & AMBER

ALL OTHER APPARATUS & EQUIPMENT MANUFACTURED TO CLIENT'S DESIGN

INDUSTRIAL & ENGINEERING APPARATUS CO. PRIVATE LTD.

CHOTANI ESTATES, PROCTOR ROAD GRANT ROAD, BOMBAY 7.

Phone : 34-3176. Telegrams : Nadiachemi.

NADIA CHEMICAL WORKS PRIVATE LTD.

C 44, 45 & 46, COLLEGE STREET MARKET, CALCUTTA-12.

Manufacturers of :-

1. *CHEMICALS*—Benzene, Toluene, etc., Bromine, Halogen derivatives of both Organic and Inorganic compounds and other fine Laboratory Chemicals

2. STILLS for distilling Essential Oils, Alcohols, Water, etc.
   RECTIFIERS, CONDENSERS, etc.

3. OVENS, Baths, etc. for Gas, Oil or Electric heatings.

4. Scientific Apparatus (PHYSICAL, CHEMICAL, BIOLOGICAL, etc.) of both Glass and Metal.

5. MICRO-ANALYSIS APPARATUS.

Please ask for Estimates.

VERY RELIABLE INDIGENOUS SUBSTITUTES OF GUARANTEED ANALYTICAL REAGENTS MAY BE FOUND IN

"BASYNTH"
Brand
ANALYTICAL REAGENT

Acid Hydrochloric
Acid Hydrochloric Fuming
Acid Sulphuric
Acid Nitric
Acid Nitric Fuming
Acid Acetic Glacial
Ammonium Hydroxide
Benzene
Toluene
Xylene
Petroleum Ether
Amyl Alcohol
Butyl Alcohol Etc., Etc.

BASIC & SYNTHETIC CHEMICALS PRIVATE LIMITED
P. O. Jadavpur University, Calcutta-32

MADE IN INDIA
HIGH VACUUM ROTARY PUMP
Single Stage & Two Stage
With or Without Air Ballast
All Indian Materials and Construction

BASIC & SYNTHETIC CHEMICALS PRIVATE LIMITED
P. O. Jadavpur University, Calcutta-32

*** FOR YOUR REQUIREMENTS**
OF ALL KINDS OF EQUIPMENTS FOR RESEARCH *

RAJ-DER-KAR & CO.,

SADHANA RAYON HOUSE, Dr. D. NAOROJI ROAD, BOMBAY-1

Branch Office :
44/6, Regal Building, Connaught Place, New Delhi.

TELEPHONE : 26-2304
TELEGRAM : TECHLAB

A few of our Agencies :

* LUDWIG SEIBOLD, Austria,
For *p*H Testers, Titrators
and Recorders, etc.

EASTMAN KODAK, U. S. A.,
For All Sorts of Complex
Organic Chemicals.

* W. A. TAYLOR & CO., U. S. A.,
For *p*H Comparators, Indicators,
Water Analysers, etc.

* TRACERLAB Inc., U. S. A.,
For Radiochemicals & Equipments
for Nuclear Research.

We Manufacture..

Laboratory Chemicals & Reagents

of a wide range under rigid control and expert supervision to ensure guaranteed standard & reliability.

A selection from our range :

*Acetone
*Alcohol Methyl
*Barium Carbonate
*Barium Chloride
*Benedicts' Solution
*Benzene
*Carbon Tetrachloride
*Lead Acetate
*Liquor Ammon Fort
*Magnesium Sulphate XL
*Xylol

THE CALCUTTA CHEMICAL CO., LTD.

HEAD OFFICE: 35, PANDITIA ROAD, CALCUTTA 29.

Branch Office & Depots at :

Delhi, Madras, Bombay, Bangalore, Vizag, Ranchi, Nagpur, Jamshedpur, Patna, Bilaspur, Bhagalpur, Madhupur, Asansol, Siliguri.

A Monumental Work *Published March 1956*

A book that should find place on the shelves of every Library

HISTORY OF CHEMISTRY IN ANCIENT & MEDIEVAL INDIA

Incorporating

HISTORY OF HINDU CHEMISTRY

by Acharya Prafulla Chandra Ray

Edited by Prof. P. Rây

Royal 8*vo*. Rexin bound, 494 pages with 39 illustrations.

Price *ex*-postage : Prime Edition : —Rs. 24/- (Inland), Ordinary Edition —Rs. 20/- (Inland)
£ 2/- or $ 6.00 (Foreign)

For Fellows „ „ Rs. 20/- „ „ Rs. 16/-

An invaluable book for students of science and history and to all persons interested in the scientific heritage of India.

PUBLISHED BY THE INDIAN CHEMICAL SOCIETY

92, Acharya Prafulla Chandra Road, Calcutta-9, INDIA.

Some Opinions :

Nature, January 5, 1957.

"Since there is much new material in the book, all those who are fortunate enough to have the earlier edition will wish to have the new one.

All those interested in the History of Chemistry owe a debt of gratitude to Prof. P. Rây and the Indian Chemical Society for its publication".

J. R. Partington.

Journal of Chemical Education, February, 1957 :

".....Professor Rây, in his carefully constructed revision of Prafulla Chandra Ray's standard 'History of Hindu Chemistry' has given us a highly informative and interesting description of Indian Chemistry. In chronological order, the contributions of Indians to chemistry have been recorded from the Harappa period of the fourth millennium B.C. to the end of Mogul culture.....Many of the ideas described make delightful reading for the average chemist with a historical bent.....chemists and historians of chemistry will find in this book a valuable assessment of ancient Indian chemistry and culture".

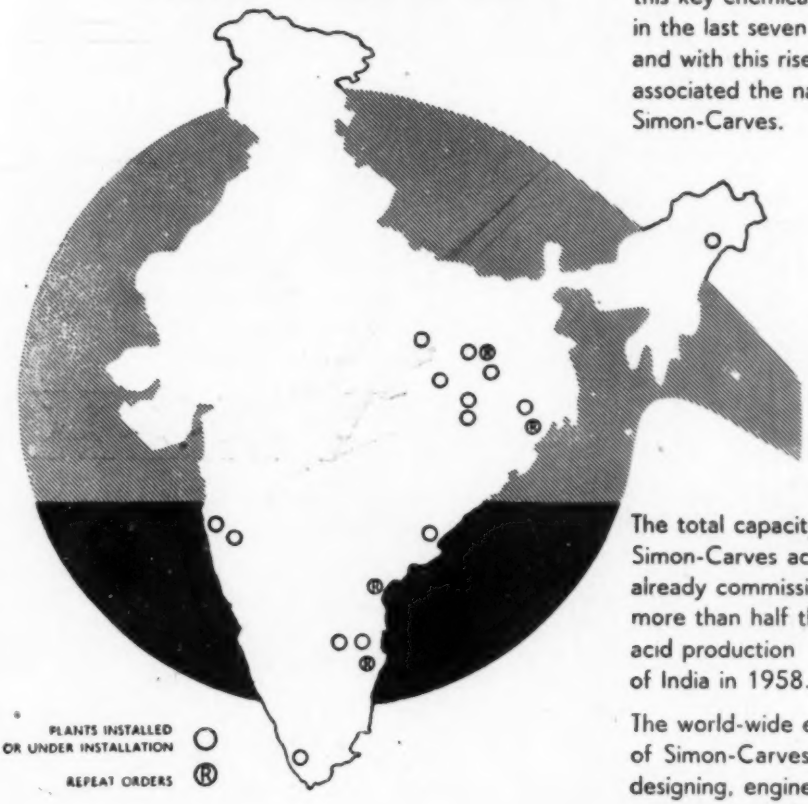
ISIS-Vol. 49, p. 362, Sept., 1958.

".....this new book is very valuable both as a re-edition of an out-of-print classic collection of fundamental data and as a presentation of much well illustrated documentation of Indian achievements in the practical arts in the field of chemistry, according to the archæological findings".

J. Filliozat.

WITH 18 SULPHURIC ACID PLANTS ALREADY INSTALLED OR UNDER INSTALLATION BY THEM, SIMON-CARVES ARE CONFIDENT OF....

THE ACID TEST



Production of Sulphuric Acid is an unfailing index of a country's industrial growth and economic independence.

There has been a threefold rise in the production of this key chemical in India in the last seven years, and with this rise is associated the name of Simon-Carves.

The total capacity of Simon-Carves acid plants already commissioned is more than half the entire acid production of India in 1958.

The world-wide experience of Simon-Carves in designing, engineering and constructing Sulphuric Acid plants, is at the service of India.

Simon-Carves Ltd

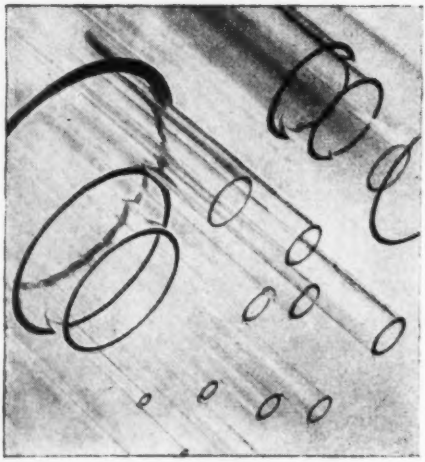
SIMON ENGINEERING GROUP

Incorporated in England. The liability of the members is limited.

32 Dalhousie Square South, Calcutta-1

SCC-17

Through thick and thin Pyrex



Everyone who makes glass apparatus needs Pyrex Tubing. The Pyrex catalogue lists no fewer than 80 standard lines, all in healthy demand. Who uses all this tubing? Hospitals, research labs for Government and industry, universities, schools. PYREX are always improving their production methods to attain even higher standards of quality. This is one good reason (among many) why everyone who is looking for quality glassware looks for PYREX

Pyrex tubing

is made from Pyrex borosilicate glass

It is therefore

heat-resistant
mechanically strong
chemically durable
—and functionally matches all other PYREX glass apparatus

In addition, its chemical composition is now completely free from arsenic

Sizes 2 mm to 100 mm o/diam—the largest size-range available in borosilicate glass

Wall Thickness Standard Wall, Heavy Wall, Extra Heavy. Also Capillary range

Length Tubing is supplied in standard lengths of approximately 5 feet

SPECIAL problems concerning manipulated tubing can be referred to the PYREX Service Department, who will gladly construct special laboratory equipment to your drawings, in consultation (if necessary) with your scientific and technical staff

•

PYREX

Regd. Trade Mark

MADE IN JP PYREX JP ENGLAND

Laboratory and scientific glass

AVAILABLE FROM ALL LEADING DISTRIBUTORS

SOLE AGENTS:

GORDHANDAS DESAI PRIVATE LTD.

PHEROZESHAH MEHTA ROAD, FORT, BOMBAY-1

Also at CALCUTTA, MADRAS & NEW DELHI

PRESIDENT :

K. VENKATARAMAN, D.Sc., F.N.I.

VICE-PRESIDENTS :

(who have filled the office of President)

P. K. BOSE, D.Sc., F.N.I.
N. R. DHAR, D.Sc., DR.ES. Sc., F.R.I.C., F.N.I.
B. C. GUHA, D.Sc., PH.D., F.N.I.
P. C. GUHA, D.Sc., F.N.I.
J. N. MUKHERJEE, C.B.E., D.Sc., F.A.S.B., F.N.I.
MATA PRASAD, D.Sc., F.R.I.C., F.N.I.
J. N. RAY, O.B.E., D.Sc., F.R.I.C., F.N.I.
P. RAY, M.A., F.N.I.
B. K. SINGH, Sc.D., F.R.I.C., F.N.I.

VICE-PRESIDENTS :

B. N. GHOSH, D.Sc., F.N.I.
P. B. SARKAR, DR.ES.Sc., F.N.I.
V. SUBRAHMANYAN, D.Sc., F.R.I.C., F.N.I.
V. M. BHAVE, M.Sc., Ph.D., A.R.I.C. President of Bombay Branch *(ex-officio)*.

HONY. SECRETARY :

M. M. CHAKRABARTY, M.Sc., PH.D.

HONY. TREASURER :

D. CHAKRAVARTI, D.Sc., F.N.I.

MEMBERS OF THE COUNCIL :

J. C. BARDHAN, D.Sc.
A. K. BHATTACHARYA, D.Sc., F.R.I.C.
MRS. ASHIMA CHATTERJEE, D.Sc.
B. CHATTERJEE, D.Sc.
A. C. CHATTERJI, D.Sc., DR. ING.
R. D. DESAI, D.Sc., F.R.I.C., F.I.I.Sc., F.A.Sc., F.N.I.
K. S. G. DOSS, D.Sc., F.N.I., F.R.I.C., F.Inst.P.
M. O. FAROOQ, M.Sc., PH.D.
T. N. GHOSH, D.Sc., F.N.I.
J. GUPTA, D.Sc.
S. M. MEHTA, B.A., M.Sc., F.A.Sc., A.R.I.C., F.N.I.
T. N. MEHTA, M.Sc., PH.D.
R. P. MITRA, D.Sc., F.N.I.
S. N. MUKHERJEE, D.Sc.
P. V. NAIR, M.Sc., D.PHIL.
B. PRASAD, D.Sc., F.N.I.
T. R. SESHADRI, M.A., PH.D., F.R.S.
R. C. SHAH, M.Sc., PH.D., F.N.I., F.R.I.C.
B. S. SRIKANTAN, D.Sc.
S. H. ZAHEER, M.A., PH.D.

HONY. EDITORS :

D. K. BANERJEE, D.Sc.
A. N. KAPPANNA, D.Sc.

BOARD OF ASSOCIATE EDITORS :

U. P. BASU, D.Sc., F.N.I.
MRS. A. CHATTERJEE, D.Sc.
B. CHATTERJEE, D.Sc.
P. C. DUTTA, D.Sc.
B. C. GUHA, D.Sc., PH.D., F.N.I.
S. S. JOSHI, D.Sc., F.N.I.
R. P. MITRA, D.Sc., F.N.I.
S. M. MUKHERJI, D.Sc., F.N.I.
S. N. MUKHERJEE, D.Sc.
P. RAY, M.A., F.N.I.
S. P. RAYCHAUDHURI, D.Sc., PH.D., F.N.I., F.R.I.C.
P. B. SARKAR, DR.ES. Sc., F.N.I.
R. C. SHAH, M.Sc., PH.D., F.N.I., F.R.I.C.
S. H. ZAHEER, M.A., PH.D.

HONY. AUDITORS :

P. C. NANDI, M.A., B.Sc., A.C.A.R.A.
A. B. GUPTA, B.Sc., L.L.B., A.C.A.R.A.

ASST. SECRETARY :
K. L. MUKHERJEE, M.Sc.

ASST. EDITOR :
G. BANERJEE, M.Sc.

Regtd. No. C 1878.

HELLIGE AQUA TESTER

FOR ANALYSES OF WATER

SEWAGE AND INDUSTRIAL WASTES.

•

Employs GUARANTEED NONFADING Glass Colour Standards for 30 tests including pH, Fluoride, Iron, Colour of Water, etc.

Approved A.P.H.A. and A.W.W.A. Methods.

Manufactured by Hellige Inc., U. S. A.

•

Sole Agents in India:

GORDHANDAS DESAI PRIVATE LIMITED

SIR PHEROZESHAH MEHTA ROAD, BOMBAY-1

Branches:

P-7, Mission Row Extension
CALCUTTA-1

4/2B, Asaf Ali Road
NEW DELHI

22, Linghi Chetty Street
MADRAS-1

SP/GD

Published by G. Banerjee, M.Sc., Asst. Editor, Indian Chemical Society, 92, Acharya Prafulla Chandra Road, Calcutta-9 and Printed by D. A. Lakin at The Statesman Press, Chowringhee Square, Calcutta-1.